Synthesis of N-Heterocyclic Carbene-Containing Metal Complexes from 2-(Pentafluorophenyl)Imidazolidines

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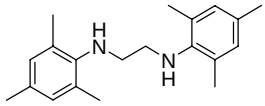
Supplemental Information

Contents

Materials and Methods

All reactions involving metal complexes were conducted under nitrogen or argon atmospheres using standard glovebox or standard Schlenk techniques. Solvents were purified by passage through alumina.[1] Resonances for NMR spectra are reported relative to Me_4Si (δ 0.0) for ^1H and ^{13}C and H_3PO_4 (δ 0.0) for ^{31}P. Spectra are reported as follows: chemical shift (δ ppm), integration, multiplicity and coupling constant (Hz). (2,6-dimethoxyphenyl)imidazoline, catalyst **2** and $RuCl_2(PCy_3)$(=CH-o-iPr-Ph) were provided by Materia, Inc. 1,3-dimesitylimidazoline,[2] *N*-2-(mesitylimino)ethylidene-2,4,6-trimethylbenzenamine,[2] 1,3-bis(2,6-diisopropyl)2-pentafluorophenyl)imidazolidine[3], and 2,4,6-trimethyl-N-(2-methylamino)ethyl)benzenamine[4] were prepared as described in the literature. All other reagents were purchased from Aldrich and used without prior purification.

I. Experimental Procedures



S1

***N*-(2-(mesitylamino)ethyl)-2,4,6-trimethylbenzenamine (S1)**

A 250 mL round bottom flask equipped with a stir bar was charged with *N*-2-(mesitylimino)ethylidene)-2,4,6-trimethylbenzenamine (2.0 g; 6.8 mmol) and sodium borohydride (1.1 g; 28 mmol), which were dissolved in 25 mL of THF at 0 °C. Concentrated HCl (1.1 mL) was added dropwise over a 30 minute period and the solution became grey in color with the evolution of gas. The reaction stirred for an additional 20 minutes and then 70 mL of 3 N HCl was added. The solution was allowed to warm to room temperature and stirred for one hour. The reaction mixture was filtered through a glass frit, and the white precipitate was washed with H_2O (2 × 25 mL) and rinsed with 40 mL of a 5% acetone:hexanes mixture. The organics were extracted with CH_2Cl_2 (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to afford a white solid. Yield: 20 %. ^1H NMR spectra match the data reported in the literature.[2]

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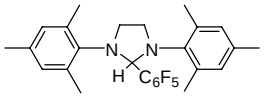
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[2] Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523–14534.

[3] Bedford, R. B.; Betham, M.; Blake, M. E.; Frost, R. M.; Horton, P. N.; Hursthouse, M. B.; López-Nicolás, R. -M. *Dalton Trans*. **2005**, 2774–2779.

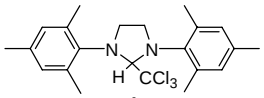
[4] Vehlow, K.; Maechling, S.; Blechert, S. *Organometallics* **2006**, *25*, 25–28.



1

1,3-dimesityl-2-(pentafluorophenyl)imidazoline (1)

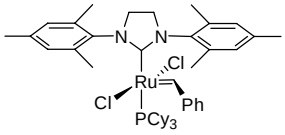
In a 10 mL flask equipped with a stir bar, **S1** (380 mg; 1.28 mmol) was dissolved in 0.7 mL of AcOH. Pentafluorobenzaldehyde (426 mg; 2.18 mmol) was then added and the reaction stirred overnight. The yellow precipitate was placed in a glass frit and washed with cold methanol to afford a white powder. Yield: 90 %. ^{1}H and ^{19}F NMR spectra match the data reported in the literature.[5] High-resolution MS analysis (FAB+) m/z: calcd 473.2016 [M+H], found 473.2007 [M+H].



4

1,3-dimesityl-2-(trichloromethyl)imidazolidine (4)

A 10 mL round bottom flask equipped with a stir bar was charged with sodium hydroxide (232 mg; 5.80 mmol). To this was added 1.45 mL of chloroform. The solution stirred for two minutes and then 1,3-dimesitylimidazoline (101 mg; 0.294 mmol) was added. The solution stirred for two hours and was poured into 30 mL of ice water. The organics were extracted with CH_2Cl_2 (2 × 20 mL), rinsed with brine, dried over $MgSO_4$(s) and concentrated under vacuum to afford a white solid. The solid was dissolved in toluene and filtered through a small silica plug with (1:20 EtOAc:hexanes) to afford a white solid. Yield: 69%. ^{1}H and ^{31}P NMR spectra match the data reported in the literature.[6]



3

$(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh (3) from 1

In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with **1** (100 mg; 0.211 mmol) and **2** (116 mg; 0.141 mmol). To this was added 4.2 mL of toluene. The vial was capped and removed from the glove box. It was then placed into an oil bath at 60 °C and stirred for four hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (8% ether:pentane) to afford a reddish-brown solid. Yield: 91%. ^{1}H and ^{31}P NMR spectra match the data reported in the literature.[7] High-resolution MS analysis (FAB+) m/z: calcd 848.3306, found 848.3322.

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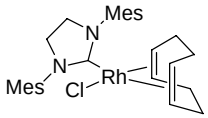
[5] Nyce, G. W.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *Chem. Eur. J.* **2004**, *10*, 4073–4079.

[6] Arduengo, A. J.; Calabrese, J. C.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348–2364.

[7] Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T. -L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546–2558.

(H_2IMes)(PCy_3)($Cl)_2$Ru=CHPh (3) from 4

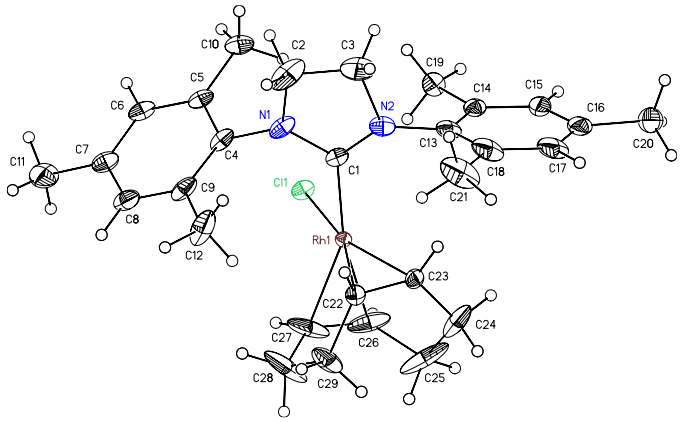
By using the procedure described to prepare **3** from **1**, the reaction of **4** (77 mg; 0.18 mmol) and **2** (100 mg; 0.12 mmol) in 3.6 mL of toluene yielded **3** as a reddish-brown solid. Yield: 87%. ^{1}H and ^{31}P NMR spectra match the data reported in the literature.[7] High-resolution MS analysis (FAB+) m/z: calcd 848.3306, found 848.3315.



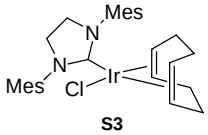
S2

Chloro(η^4-1,5-cyclooctadiene)(1,3-dimesitylimidazole-2-ylidene)rhodium(I) (S2)

In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with $[Rh(cod)Cl]_2$ (25 mg; 0.050 mmol) and **1** (0.048 mg; 0.10 mmol). To this was added 2.0 mL of toluene. The vial was capped and removed from the glove box. It was then placed into an oil bath at 70 °C and stirred for two hours. The reaction mixture was purified by flash column chromatography on silica gel (50% ether:hexanes) to afford a yellow crystalline solid. Yield: 90%. ^{1}H NMR and ^{13}C NMR data ($CDCl_3$) are reported for **S2** in the literature[8], however, in our hands we found different data. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.98 (4H, d, J = 14.9 Hz, *m*-H), 4.45 (2H, s, cod_{vinyl}), 3.84 (4H, m, J= 6.6, 2.0 Hz, NCH_2CH_2N), 3.35 (2H, s, cod_{vinyl}), 2.58 (6H, s, *p*-CH_3), 2.31 (12H, d, J= 7.15 Hz, *o*-CH_3), 1.75 (4H, m, J= 5.5 Hz, cod_{alkyl}), 1.49 (4H, m, J= 4.1 Hz, cod_{alkyl}). ^{13}C NMR (75MHz, $CDCl_3$, 298 K) δ 212.39 (d, J= 48.7 Hz, *C*–Rh), 137.9 (*p*-Ph), 136.0 (*o*-Ph), 134.9 (*m*-Ph), 129.7 (NCH_2CH_2N), 128.1 (NCH_2CH_2N), 96.9 (cod), 67.3 (cod), 51.1 (cod), 32.4 (cod), 27.9 (cod), 20.8 (cod), 19.7 (*o*-CH_3), 18.1 (*p*-CH_3). High-resolution MS analysis (FAB+) m/z: calcd 552.1778, found 552.1762. X-Ray crystal structure confirms connectivity (Section III).



S2



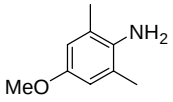
S3

Chloro(η^4-1,5-cyclooctadiene)(1,3-dimesitylimidazole-2-ylidene)iridium(I) (S3)

By using the procedure described to prepare (**S2**), the reaction of $[Ir(cod)Cl]_2$ (71 mg; 0.15 mmol) and **1** (50 mg; 0.74 mmol) in 3.0 mL of toluene yielded the product as an orange solid. The resulting reaction mixture was purified by flash column chromatography on silica gel (30% ether:hexanes) to afford an orange crystalline solid. Yield: 89%. ^{1}H NMR and ^{13}C NMR data ($CDCl_3$) are reported for **S3** in the literature[8], however, in our hands we found different data. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.94 (4H, d, J=10.7 Hz, *m*-H), 4.07 (2H, m, cod_{vinyl}), 3.88

[8] Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem*. **2002**, *649*, 219–224.

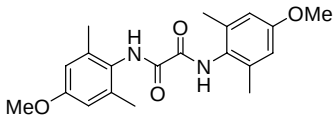
(4H, s, NCH_2CH_2N), 3.06 (2H, m, cod $_{vinyl}$), 2.53 (6H, s, *p*-CH_3), 2.31 (12H, d, J= 9.07 Hz, *o*-CH_3), 1.62 (4H, m, cod$_{alkyl}$), 1.26 (4H, m, cod$_{alkyl}$). ^{13}C NMR (75MHz, $CDCl_3$, 298 K) δ 207.4 (*C*–Ir), 138.1 (*p*-Ph), 136.4 (*o*-Ph), 135.5 (*m*-Ph), 130.0 (NCH_2*C*H_2N), 128.6 (NCH_2CH_2N), 83.9 (cod), 51.9 (cod), 51.7 (cod), 33.6 (cod), 28.9 (cod), 21.3 (cod), 20.1 (*o*-*C*H_3), 18.7 (*p*-*C*H_3). High-resolution MS analysis (FAB+) m/z: calcd 642.2352 ([M]$^+$), found 642.2347 ([M]$^+$).



S4

4-methoxy-2,6-dimethylaniline (S4)

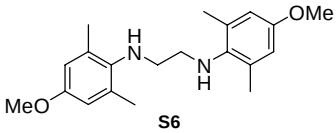
A dry, two-neck 100 mL round bottom flask equipped with a stir bar was charged with 4-amino-3,5-dimethylphenol (2.02 g; 14.8 mmol) and iodomethane (2.21 g; 15.6 mmol) under Ar(g). DMF (44 mL) was added and the reaction stirred at room temperature under Ar(g) for ten minutes to afford a dark solution. Potassium tertbutoxide (2.50 g; 22.3 mmol) was added and the solution became tan and eventually dark green in color. The reaction stirred for a total of 16 hours and was then suspended in CH_2Cl_2. The organics were washed with 1 N KOH (3 × 50 mL) and brine, dried over $MgSO_4$(s) and concentrated under vacuum to yield a yellow solid. The crude product (with excess DMF) was used in the next reaction without characterization.



S5

***N*^{1},*N*^{2}-bis(4-methoxy-2,6-dimethylphenyl)oxalamide (S5)**

In a 250 mL erlenmeyer flask, sodium hydroxide (1.8 g, 45 mmol) was dissolved in 75 mL of H_2O. The solution was placed into an ice bath and **S4** (2.24 g; 14.8 mmol) was added. Oxalyl chloride (1.05 mL; 12.0 mmol) was then added slowly by syringe. Gas evolved and a light brown precipitate formed instantaneously. The crude product was used in the next reaction without characterization. Yield: 19% over two steps.

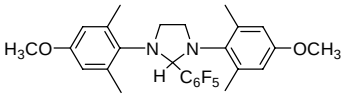


S6

***N*-(2-(4-methoxy-2,6-dimethylphenylamino)ethyl)-4-methoxy-2,6-dimethylbenzenamine(S6)**

A 100 mL pressure tube equipped with a stir bar was charged with **S5** (0.50 g; 1.4 mmol) under Ar(g). To this was added 12 mL of BH_3·THF (1.0 M in THF). The reaction vessel was capped and placed into an oil bath at 75 ºC behind a safety shield. The solution was stirred for 16 hours at this temperature. The reaction was allowed to cool to room temperature and poured into 20 mL of MeOH in a 100 mL round bottom flask. Then, 0.50 mL of HCl was added. A precipitate formed and the solution was concentrated under vacuum to reveal a white solid. The solid was redissolved in methanol and concentrated to dryness two more times. The white solid was suspended in CH_2Cl_2 and 2 N KOH. The organics were extracted with CH_2Cl_2 (3 × 25 mL), washed with brine, dried over $MgSO_4$(s) and concentrated under vacuum to afford an off-white

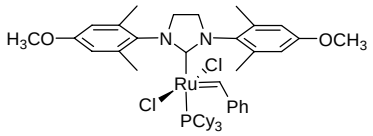
powder. Yield: 63%. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 6.79 (4H, s, *m*-H), 3.54 (6H, s, OCH_3), 3.02 (4H, s, NCH_2CH_2N), 2.32 (12H, s, *o*-CH_3). ^{13}C NMR (75MHz, C_6D_6, 298 K) δ 155.8 (*p*-C), 139.8 (*C*(Ar)–N), 132.3 (*o*-C), 114.5 (*m*-C), 55.0 (OCH_3), 49.9 (NCH_2CH_2N), 18.7 (*o*-CH_3). High-resolution MS analysis (FAB+) m/z: calcd 328.2151 ($[M]^+$), found 328.2150 ($[M]^+$).



S7

1,3-Bis(4-methoxy-2,6-dimethylphenyl)-2-(pentafluorophenyl)imidzolidine (S7)

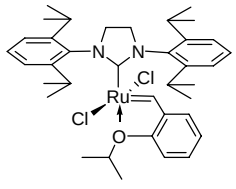
In a 10 mL round bottom flask equipped with a stir bar, **S6** (68 mg; 0.18 mmol) was suspended/ dissolved in 0.7 mL of secBuOH. Pentafluorobenzaldehyde (61 mg; 0.31 mmol) was then added and the reaction stirred for two hours at room temperature. The reaction mixture was suspended in hexanes and 2 N KOH. The organics were extracted with hexanes (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to afford a yellow oil. The oil was purified by flash column chromatography on Brockmann IV alumina. Yield: 87%. ^{1}H NMR (crude) (300MHz, C_6D_6, 298 K) δ 6.54 (4H, b, *m*-H), 3.68 (2H, m, NCH_2CH_2N), 3.25 (8H, m, NCH_2CH_2N and OCH_3), 2.21 (12H, b, *o*-CH_3). ^{19}F NMR (282MHz, C_6D_6, 298 K) δ –137.3 (1F, J= 14.48, 8.28 Hz), –150.3 (1F, J= 16.55, 6.21 Hz), –155.5 (1F, J= 22.8, 20.7 Hz), –162.7 (1F, J= 14.48, 8.28 Hz), –164.5 (1F, J= 14.48, 8.28 Hz). High-resolution MS analysis (FAB+) m/z: calcd 506.1993, found 506.2002.



S8

$RuCl_2$(1,3-Bis(4-methoxy-2,6-dimethylphenyl)-2-ylidene)(PCy_3)(=CHPh) (S8)

In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with **S7** (35 mg; 0.068 mmol) and **2** (28 mg; 0.034 mmol). To this was added 1.4 mL of toluene. The purple solution was then transferred into a screw-top NMR tube, removed from the glove box and then placed into an oil bath at 60 ºC for 4 hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (20% ether:pentane) to afford a reddish-brown solid. Yield: 75%. ^{1}H NMR (300MHz, CD_2Cl_2, 298 K) δ 19.1 (1H, s), 6.8-5.4 (9H, m), 3.9-3.4 (10H, m), 1.6-1.0 (45H, m). ^{31}P NMR (121MHz, CD_2Cl_2, 298 K) δ 29.8. High-resolution MS analysis (FAB+) m/z: calcd 880.3205, found 880.3208.

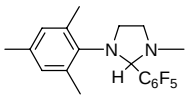


S9

$RuCl_2$(1,3-Bis(2,6diisopropylphenyl)-2-ylidene)(=CH-o-iPr-Ph) (S9)

In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with 1,3-bis(2,6-diisopropyl)-2-(pentafluorophenyl)imidazolidine (82 mg; 0.15 mmol) and $RuCl_2$(PCy_3)(=CH-o-

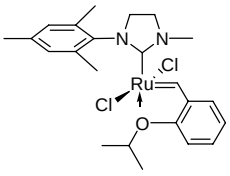
iPr-Ph) (0.59 mg; 0.097 mmol). To this was added 3.0 mL of toluene. The vial was capped and removed from the glove box. It was then placed into an oil bath at 60 °C and stirred for five hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (5% ether:hexanes) to afford a green solid. Yield: 80%. ^{1}H NMR and ^{13}C NMR data (C_6D_6) are reported for **S9** in the literature[9], however, in our hands we found different data. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 16.5 (1H, s, Ru=C*H*Ph), 7.35 (2H, J= 6.58 Hz), 7.24 (4H, m, J= 7.02 Hz), 6.58 (2H, m, J= 7.45 Hz), 6.57 (1H, t, J= 7.45 Hz), 6.26 (1H, d, J= 8.78 Hz) 4.38 (1H, sept, OC*H*$(CH_3)_2$), 3.80 (8H, m, NCH_2CH_2N and ArC*H*$(CH_3)_2$), 1.15 (6H, d, J= 7.02 Hz), 0.89 (24H, d, J= 6.14 Hz) ^{13}C NMR (75MHz, C_6D_6, 298 K) δ 287.0 (*C*–Ru), 215.5, 153.0, 149.6, 144.8,137.5, 130.0, 129.1, 124.7, 122.4, 122,2, 113.2, 71.1, 54.9, 30.2, 29.2, 26.7, 23.9, 21.8. High-resolution MS analysis (FAB+) m/z: calcd 710.2344 ($[M]^+$), found 710.2371 ($[M]^+$).



S10

1-Mesityl-3-methyl-2-(pentafluorophenyl)imidzolidine (S10)

In a 10 mL flask equipped with a stir bar, 2,4,6-trimethyl-N-(2-(methylamino)ethyl)benzenamine (207 mg; 1.08 mmol) was dissolved in 0.9 mL of AcOH. Pentafluorobenzaldehyde (359 mg; 1.82 mmol) was then added and the reaction mixture stirred for 1 hr at room temperature. The yellow solution was suspended in 50 mL of 2 N KOH and 50 mL of hexanes. The organics were extracted with hexanes (3 × 25 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to yield a yellow oil. The yellow oil was purified by flash column chromatography (5% EtOAc:hexanes) on Brockmann IV alumina and concentrated under vaccum to afford a light yellow oil. Yield: 85 %. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 6.7 (2H, s, *m*-H), 5.4 (1H, s, NC*H*(C_6F_5)N), 3.5 (2H, m, J= 6.4 Hz, NCH_2CH_2N), 3.0 (3H, m, NCH_3), 2.7 (2H, m, NCH_2CH_2N), 2.18 (3H, s, *p*-CH_3), 2.02 (6H, d, 15.0 Hz, *o*-CH_3). ^{19}F NMR (282MHz, C_6D_6, 298 K) δ −143.0 (2F, b), −155.8 (1F, t, J= 20.7 Hz), −163.3 (2F, dd, J= 14.5, 8.3 Hz). High-resolution MS analysis (FAB+) m/z: calcd 369.1390 ($[M]^+$), found 369.1393 ($[M]^+$).



S11

$RuCl_2$(1-mesityl-3-methyl-2-ylidene)(=CH-o-iPr-Ph) (S11)

S10 (113 mg; 0.304 mmol) was added to a 10 mL round bottom flask and dissolved in degassed toluene (6 mL). Ar(g) was then bubbled through the solution via syringe for 20 minutes. A separate 50 ml round bottom Schlenk flask containing $RuCl_2(PCy_3)$(=CH-o-iPr-Ph) (122 mg; 0.203 mmol) was equipped with a stir bar and removed from the glove box. It was then placed under Ar(g) (via pump/backfill × 3). To this second flask was added the solution containing 2,4,6-trimethyl-N-(2-(methylamino)ethyl)benzenamine via syringe. The flask was sealed and placed in an oil bath at 60 °C for 5 hours with stirring. The flask was cooled to room temperature and then placed under Ar(g) (pump/backfill × 3). Copper(I) chloride (20.0 mg;

[9] Courchay, F. C.; Sworen, J. C.; Wagener, K. B. *Macromolecules* **2003**, *36*, 8231–8239.

0.203 mmol) was then added and the resulting solution was allowed to stir for 1 hr at room temperature. The reaction mixture was purified by flash column chromatography (3% MeOH:CH_2Cl_2) on TSI Scientific silica gel and concentrated under vacuum to afford a green solid. Yield: 65%. ^{1}H and ^{13}C NMR spectra match the data reported in the literature.[10] High-resolution MS analysis (FAB+) m/z: calcd 522.0779, found 522.0759.

S12

***N*-(2-(2,6-dimethoxyphenylamino)ethyl)-2,6-dimethoxybenzenamine (S12)**

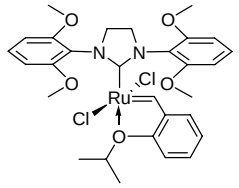
A two-neck 100 mL round bottom flask equipped with a stir bar and condenser was charged with 1,3-(2,6-dimethoxyphenyl)imidazoline (172 mg; 0.452 mmol). To this was added 30 mL of 3 N HCl. The mixture was placed in an oil bath at 80 °C and stirred for 12 hours. The solution was then cooled to room temperature and suspended in CH_2Cl_2 and 2 N KOH. The organics were extracted with CH_2Cl_2 (3 × 25 mL), washed with brine, dried over $MgSO_4$(s) and concentrated under vacuum. The resulting yellow oil was then purified by flash column chromatography on Brockmann IV alumina (0.5% EtOAc: hexanes) Yield: 41 %. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.82 (2H, t, J= 7.98 Hz, *p*-H), 6.54 (4H, d, J= 8.25 Hz, *m*-H), 4.24 (2H, s, N*H*), 3.82 (12H, s, OCH_3), 3.28 (4H, NCH_2CH_2N). ^{13}C NMR (75MHz, $CDCl_3$, 298 K) δ 151.6 (*o*-C), 126.7 (*p*-C), 120.2 (*C*(Ar)–N), 104.6 (*m*-C), 55.9 (O*C*H_3), 47.0 (N*C*H_2*C*H_2N). High-resolution MS analysis (FAB+) m/z: calcd 333.1814 ([M+H]), found 333.1806 ([M+H]).

S13

1,3-Bis(2,6-dimethoxyphenyl)-2-(pentafluorophenyl)imidzolidine (S13)

In a 10 mL round bottom flask equpped with a stir bar, **S12** (60.8 mg; 0.183 mmol) was suspended/dissolved in 0.7 mL of secBuOH. Pentafluorobenzaldehyde (61.0 mg; 0.311 mmol) was then added and the reaction stirred for 12 hours at room temperature. The reaction mixture was suspended in hexanes and 2 N KOH. The organics were extracted with hexanes (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to afford a yellow oil. The oil was purified by flash column chromatography on Brockmann IV alumina (1% methanol:CH_2Cl_2) to afford a yellow solid. Yield: 70 %. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 6.83 (2H, t, J= 10.1 Hz, *p*-H), 6.25 (4H, d, J= 8.25, *m*-H), 4.11 (2H, m, NCH_2CH_2N), 3.64 (2H, m, NCH_2CH_2N), 3.34 (12H, s, OCH_3). ^{19}F NMR (282 MHz, C_6D_6, 298 K) δ –158.8 (2F, m, J= 20.69 Hz), –166.6 (3F, m, J= 14.48, 6.21 Hz). High-resolution MS analysis (FAB+) m/z: calcd 511.1656 ([M+H]), found 511.1649 ([M+H]).

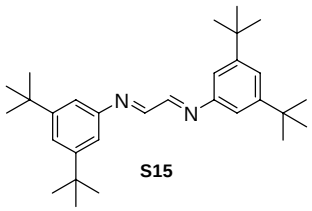
[10] Vehlow, K.; Maechling, S.; Blechert, S. *Organometallics* **2006**, *25*, 25–28.



S14

$RuCl_2$(1-mesityl-3-methyl-2-ylidene)(=CH-o-iPr-Ph) (S14)

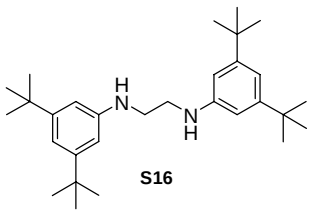
In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with **S13** (10 mg; 0.020 mmol) and $RuCl_2(PCy_3)$(=CH-o-iPr-Ph) (7.8 mg; 0.013 mmol). To this was added 0.5 mL of toluene. The brown solution was then transferred into a screw-top NMR tube, removed from the glove box and then placed into an oil bath at 60 °C for 4 hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (20% ether:pentane) to yield an olive-green solid. Yield: 25%. ^{1}H NMR (300MHz, CD_2Cl_2, 298 K) δ 18.4 (1H, s), 7.9-6.3 (10H), 5.0 (1H, sept, J= 6.4, 3.84 Hz), 4.2-3.6 (16H), 1.5 (6H). High-resolution MS analysis (FAB+) m/z: calcd 662.0889, found 662.0872.



S15

***N*-2-(3,5-di-*tert*-butylphenylimino)ethylidene)-3,5-di-*tert*-butylbenzenamine (S15)**

3,5-di-*tert*-butylaniline (2.50g; 12.2 mmol) was added to a 100 mL round bottom flask equipped with a stir bar and dissolved in a 1:1 mixiture of isopropanol:water at 0 °C. Glyoxal (40% in H_2O) (0.7 mL; 6.1 mmol) was added. The solution was stirred vigoursly for 2.5 hours and allowed to warm to room temperature. The yellow precipitate was dissolved in CH_2Cl_2 and passed through a glass frit. The yellow solution contained in the receiving flask was concentrated under vacuum to afford a yellow solid that was used in the next reaction without characterization.

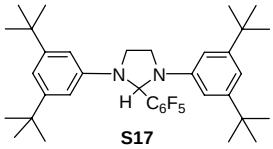


S16

***N*-(2-(3,5-di-*tert*-butylphenylamino)ethyl)-3,5-di-*tert*-butylbenzenamine (S16)**

A 10 mL round bottom flask equipped with a stir bar was charged with **S15** (2.86 g; 6.62 mmol) and sodium borohydride (1.02 g; 27.0 mmol), which were dissolved in 24 mL of THF at 0 °C. Concentrated HCl (1.09 mL) was added dropwise over a 30 minute period and the solution became grey in color with gas evolution. The solution stirred for an additional 20 minutes and 67 mL of 3 N HCl was added. The solution was allowed to warm to room temperature and stirred for one hour. The reaction mixture was filtered through a glass frit and the white precipitate was washed with H_2O (2 × 25 mL) and rinsed with 40 mL of a 5% acetone:hexanes mixture. The percipitate was suspended in CH_2Cl_2 and 2 N KOH. The organics were extracted with CH_2Cl_2 (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under

vacuum to afford a white solid. Yield: 10 %. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.60 (2H, s, *p*-H), 6.39 (4H, s, *o*-H), 5.42 (2H, s, N*H*), 3.21 (4H, s, NCH_2CH_2N), 1.21 (36H, s, CH_3).



S17

1,3-Bis(3,5-di-*tert*-butylphenyl)-2-(pentafluorophenyl)imidzolidine (S17)
In a 10 mL flask equipped with a stir bar, **S16** (181 mg; 0.416 mmol) was dissolved in 0.7 mL of AcOH. Pentafluorobenzaldehyde (170 mg; 0.867 mmol) was then added and a yellow precipitate began to form instantaneously. The reaction mixture stirred for 90 minutes. The precipitate was placed in a glass frit and washed with cold methanol to afford a white powder. Yield: 52 %. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.88 (2H, s, *p*-H), 6.52 (4H, s, *o*-H), 5.30 (1H, s, N*H*), 4.00 (2H, m, NCH_2CH_2N), 3.79 (2H, m, NCH_2CH_2N) 1.6-1.3 (36H, m, CH_3) . ^{19}F NMR (282 MHz, $CDCl_3$, 298 K) δ –142.0 (2F, b), –154.3 (1F, t, J= 21.4 Hz), –162.9 (2F, b).

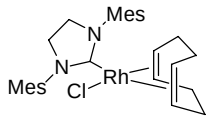
Solvent dependence of the thermolysis of 1
To evaluate the dependence of the thermolysis of **1** on the solvent composition, six 5 mL scintillation vials were charged with 20 mg of **1**. A different solvent (benzene-d_6, toluene-d_8, CD_2Cl_2, THF-d_8, acetone-d_6 or acetonitrile-d_3) was added to each vial. The vials were shaken until all of **1** dissolved. The solutions were then transferred into six screw-cap NMR tubes, which were immediately placed into an oil bath at 45 °C. After 1 hr, the NMR tubes were removed from the bath, cooled to-78 °C and ^{19}F NMR spectra were taken immediately.

^{19}F NMR data for **1**: (282 MHz, C_6D_6, 298 K) δ –137.6 (1F, m, J= 14.5, 8.3, 6.2 Hz), –150.4 (1F, m, J= 14.5, 8.3 Hz), –155.5 (1F, m, J= 22.8, 20.2 Hz), –162.7 (1F, m), –164.5 (1F, m, J= 14.5, 8.3, 6.2 Hz). ^{19}F NMR (282 MHz, THF-d_8, 298 K) δ –140.6 (1F, m, J= 12.4, 10.2, 8.3 Hz), –151.1 (1F, m, J= 14.5, 8.3 Hz), –158.1 (1F, m, J= 20.7 Hz), –165.4 (2F, m). ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) δ –136.9 (1F, m, J= 14.5, 8.3 Hz), –150.1 (1F, m, J= 14.5, 8.3 Hz), –157.3 (1F, m, J= 20.7 Hz), –164.4 (2F, m). ^{19}F NMR (282 MHz, CD_3CN, 298 K) δ –135.9 (1F, m, J= 10.3, 8.3 Hz), –151.9 (1F, m, J= 14.5, 8.3 Hz), –157.5 (1F, m, J= 20.7 Hz), –164.8 (1F, m), –165.8 (1F, m, J= 15.3, 6.1 Hz). ^{19}F NMR (282 MHz, acetone-d_6, 298 K) δ –137.4 (1F, m, J= 21.4, 9.1 Hz), –151.3 (1F, m, J= 15.3, 9.2 Hz), –157.9 (1F, m, J= 21.4, 18.3 Hz), –165.3 (1F, m, J= 21.4, 9.2 Hz), –165.7 (1F, m, J= 15.3, 6.1 Hz). ^{19}F NMR (282 MHz, toluene-d_8, 298 K) δ –137.4 (1F, m, J= 14.5, 7.3 Hz), –150.3 (1F, m, J= 14.5, 9.7 Hz), –155.9 (1F, m, J= 21.8 Hz), –163.2 (1F, m, J= 12.1, 9.7 Hz), –164.5 (1F, m, J= 20.7 Hz).

^{19}F NMR data for pentafluorobenzene: (282 MHz, C_6D_6, 298 K) δ –139.5 (2F, m, J=10.3, 8.3 Hz), –154.4 (1F, t, J= 20.7 Hz), –162.7 (2F, m). ^{19}F NMR (282 MHz, THF-d_8, 298 K) δ –137.5 (2F, m, J= 14.5, 8.3 Hz), –156.7 (1F, t, J= 20.7, 18.6 Hz), –164.5 (1F, m, J= 8.3, 6.3 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) δ –136.9 (1F, m, J= 14.5, 8.3 Hz), –150.1 (1F, m, J= 14.5, 8.3 Hz), –157.3 (1F, m, J= 20.7 Hz), –164.4 (1F, m). ^{19}F NMR (282 MHz, CD_3CN, 298 K) δ –141.1 (1F, m, J= 12.4, 10.3 Hz), –141.4 (1F, m, J= 12.4, 8.3 Hz), –156.7 (1F, m, J= 20.7, 18.6 Hz), –164.6 (2F, m). ^{19}F NMR (282 MHz, acetone-d_6, 298 K) δ –140.9 (1F, m, J= 10.3, 8.3 Hz),

–141.2 (1F, m, J= 12.4, 8.3 Hz), –156.8 (1F, m, J= 20.7, 18.6 Hz), –164.7 (2F, m).^{19}F NMR (282 MHz, toluene-d_8, 298 K) δ –139.6 (2F, m, J= 12.1, 9.7 Hz), –154.6 (1F, m, J= 21.8, 19.3 Hz), –162.8 (2F, m, J= 14.5, 7.3 Hz).

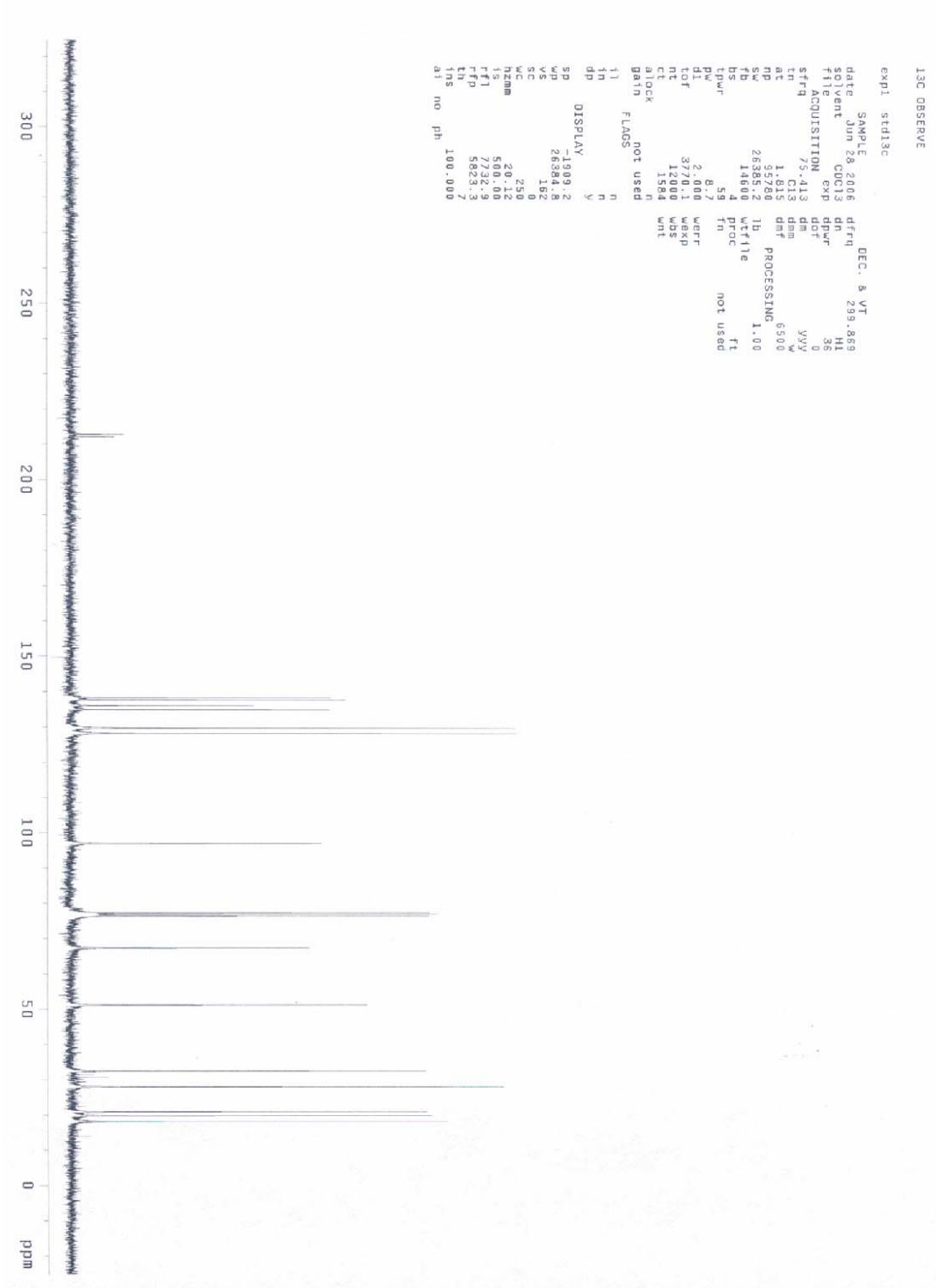
II. NMR Data

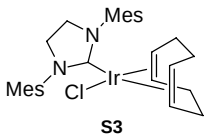


S2

^{1}H NMR Spectrum of **S2** ($CDCl_3$):

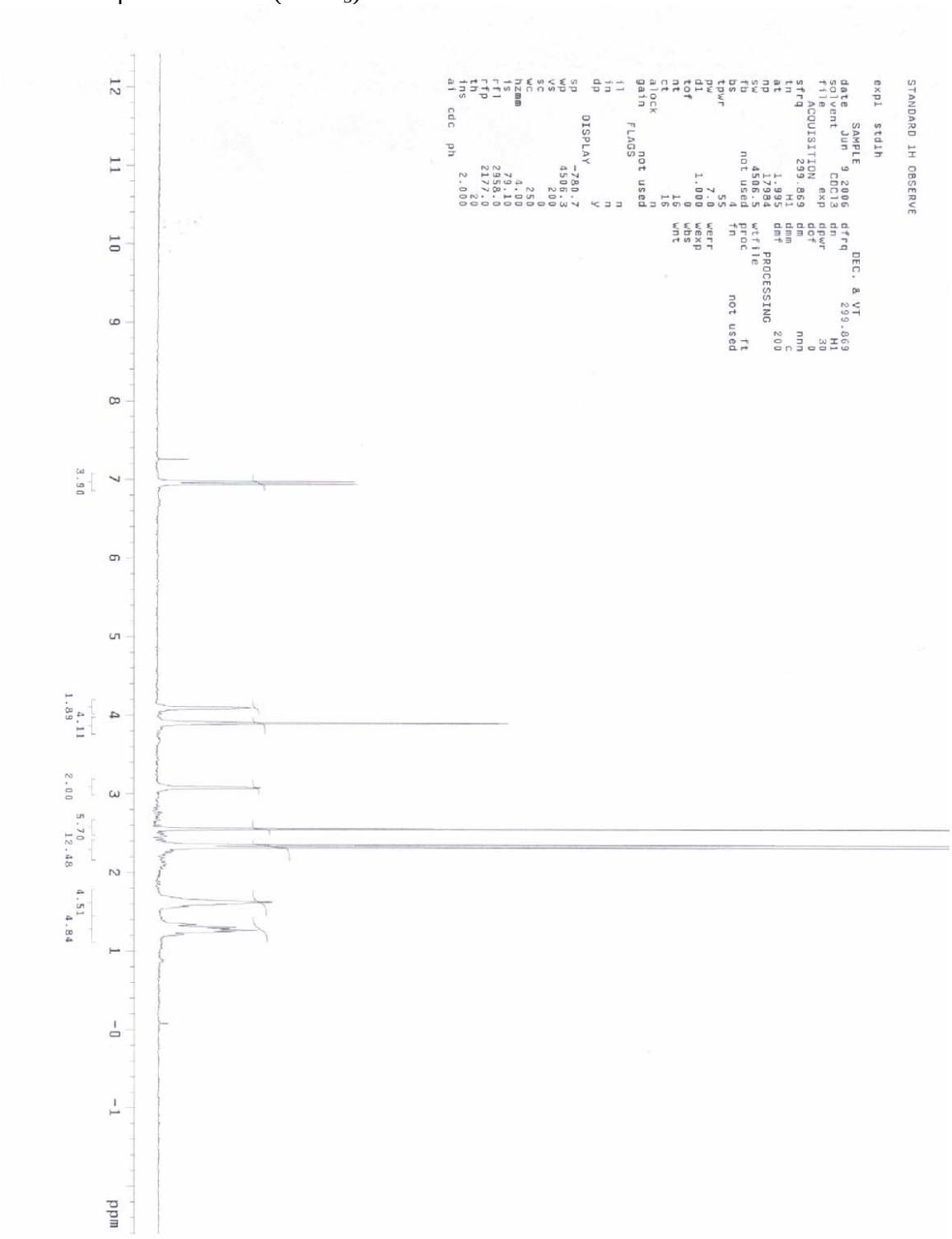
^{13}C NMR Spectrum of **S2** ($CDCl_3$):



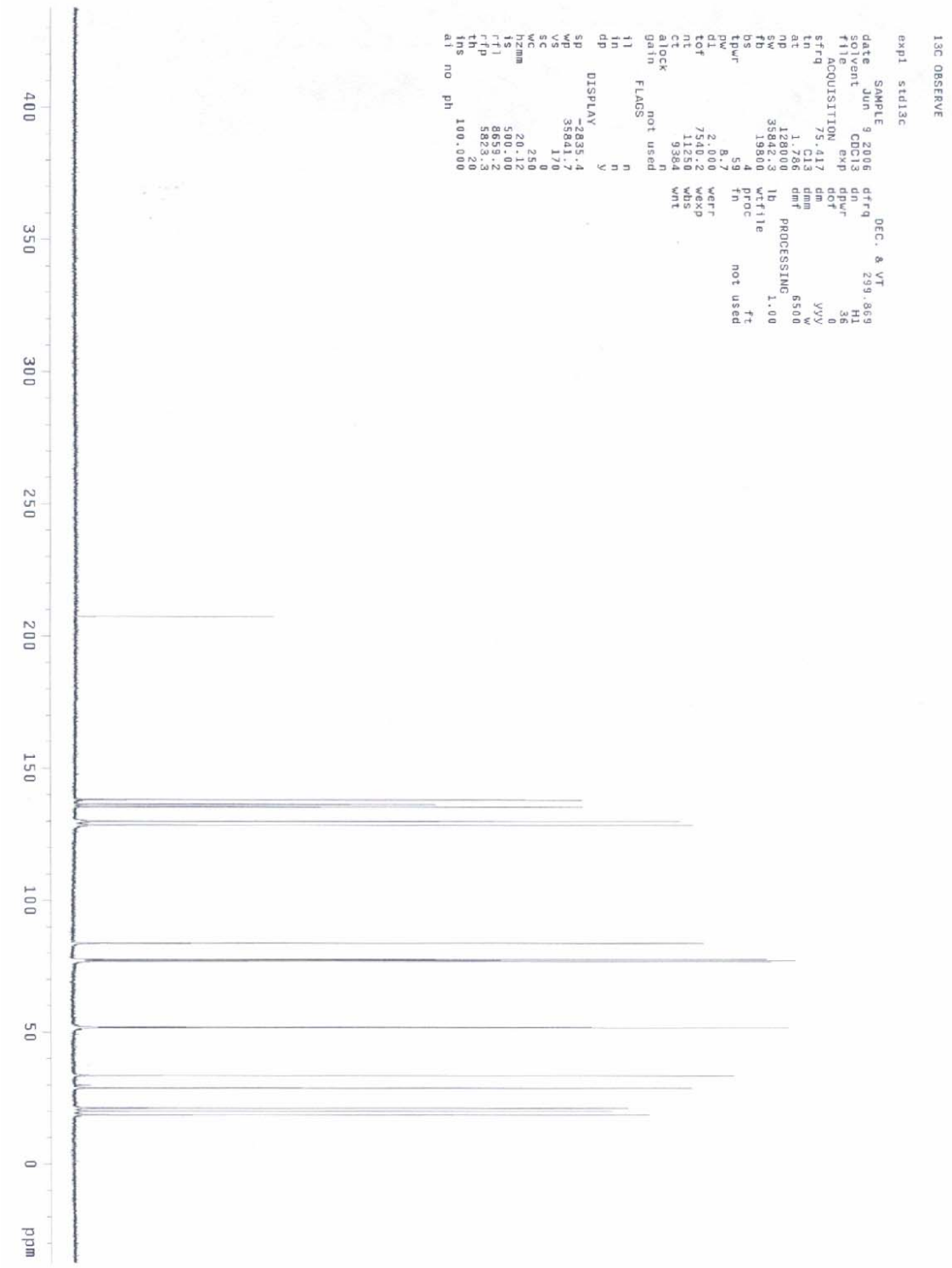


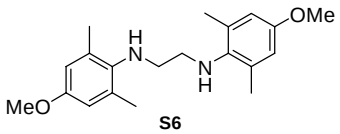
S3

^{1}H NMR Spectrum of **S3** ($CDCl_3$):



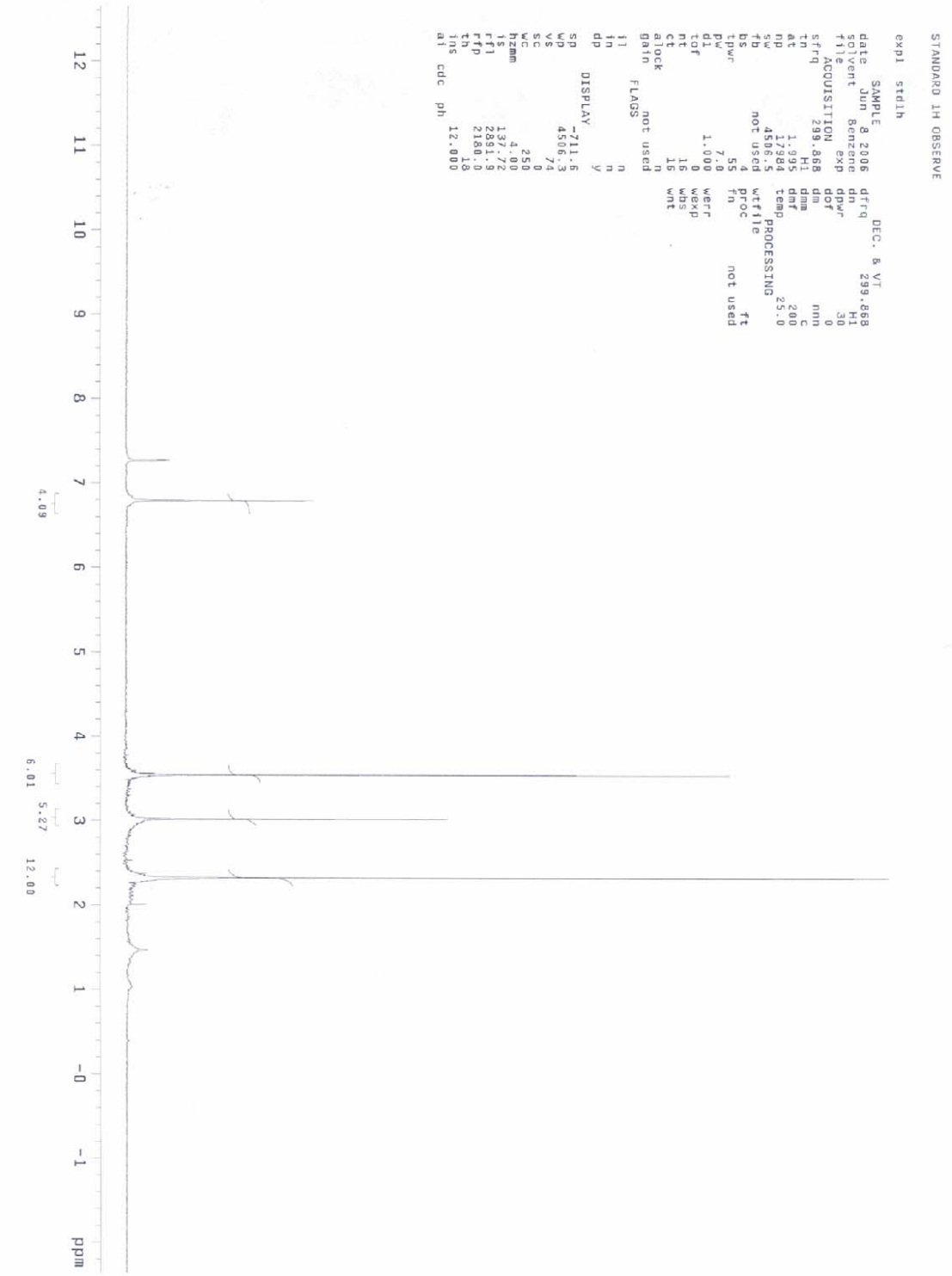
^{13}C NMR Spectrum of **S3** ($CDCl_3$):



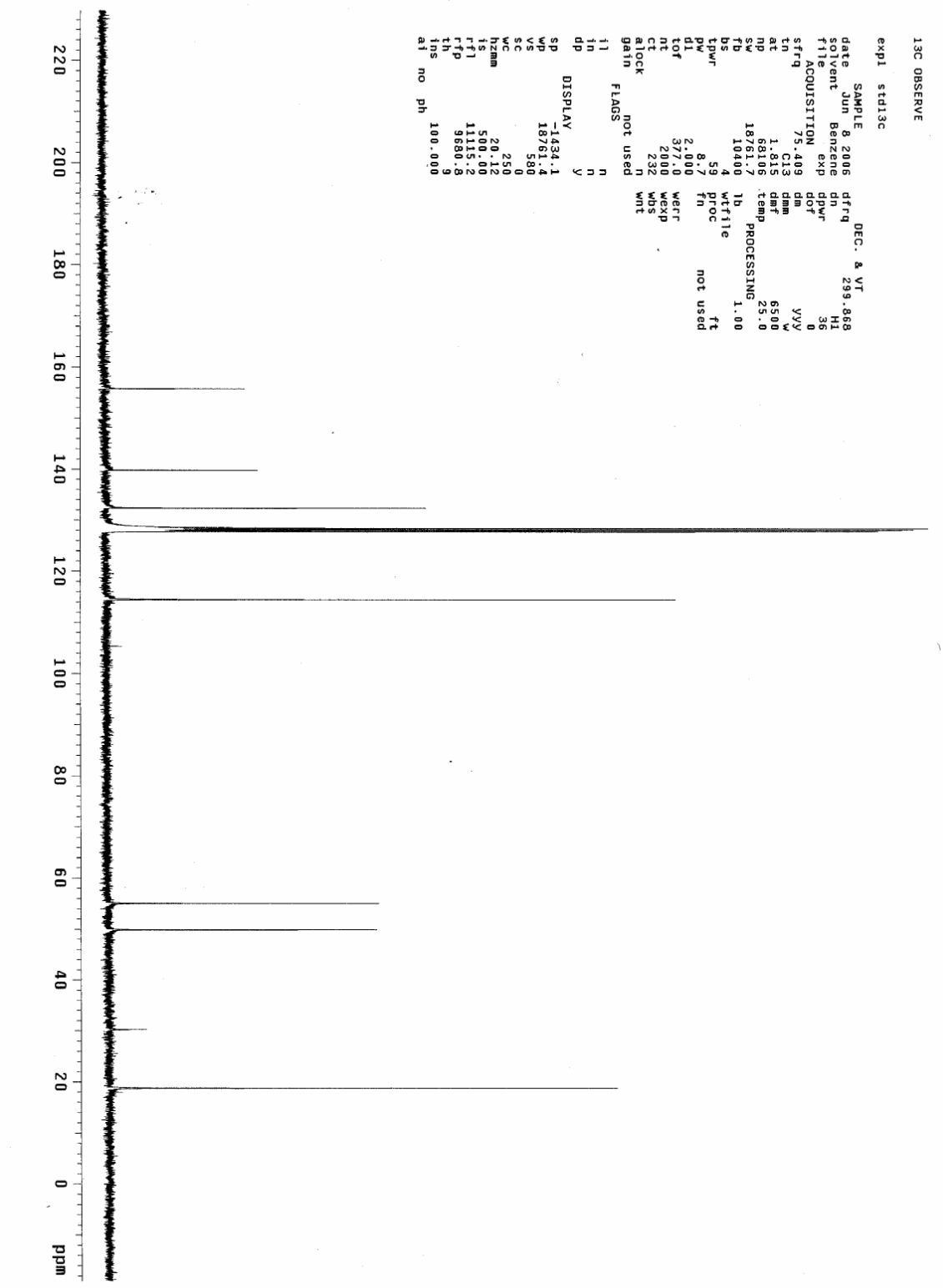


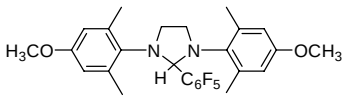
S6

^{1}H NMR Spectrum of **S6** (C_6D_6):



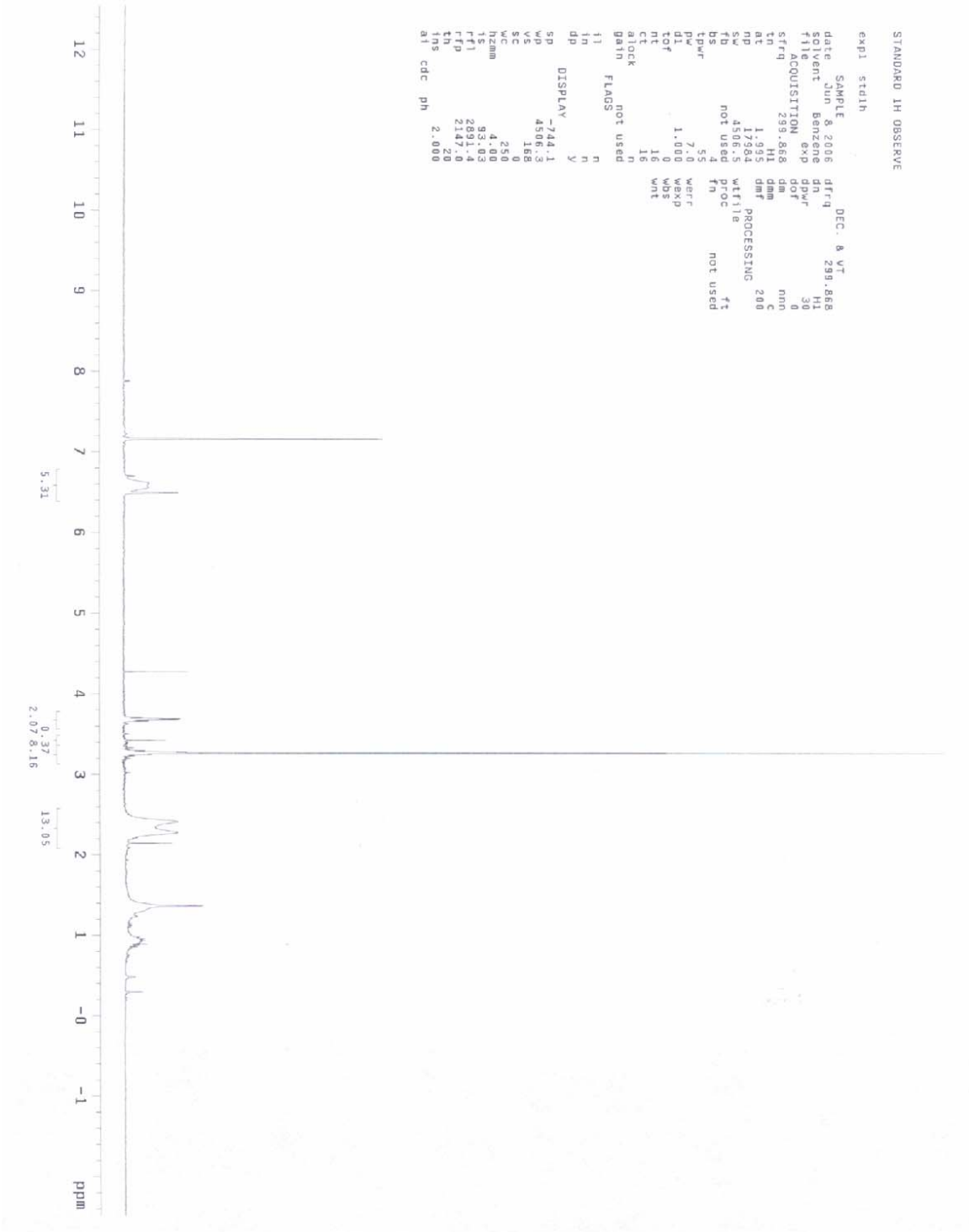
^{13}C NMR Spectrum of **S6** (C_6D_6):



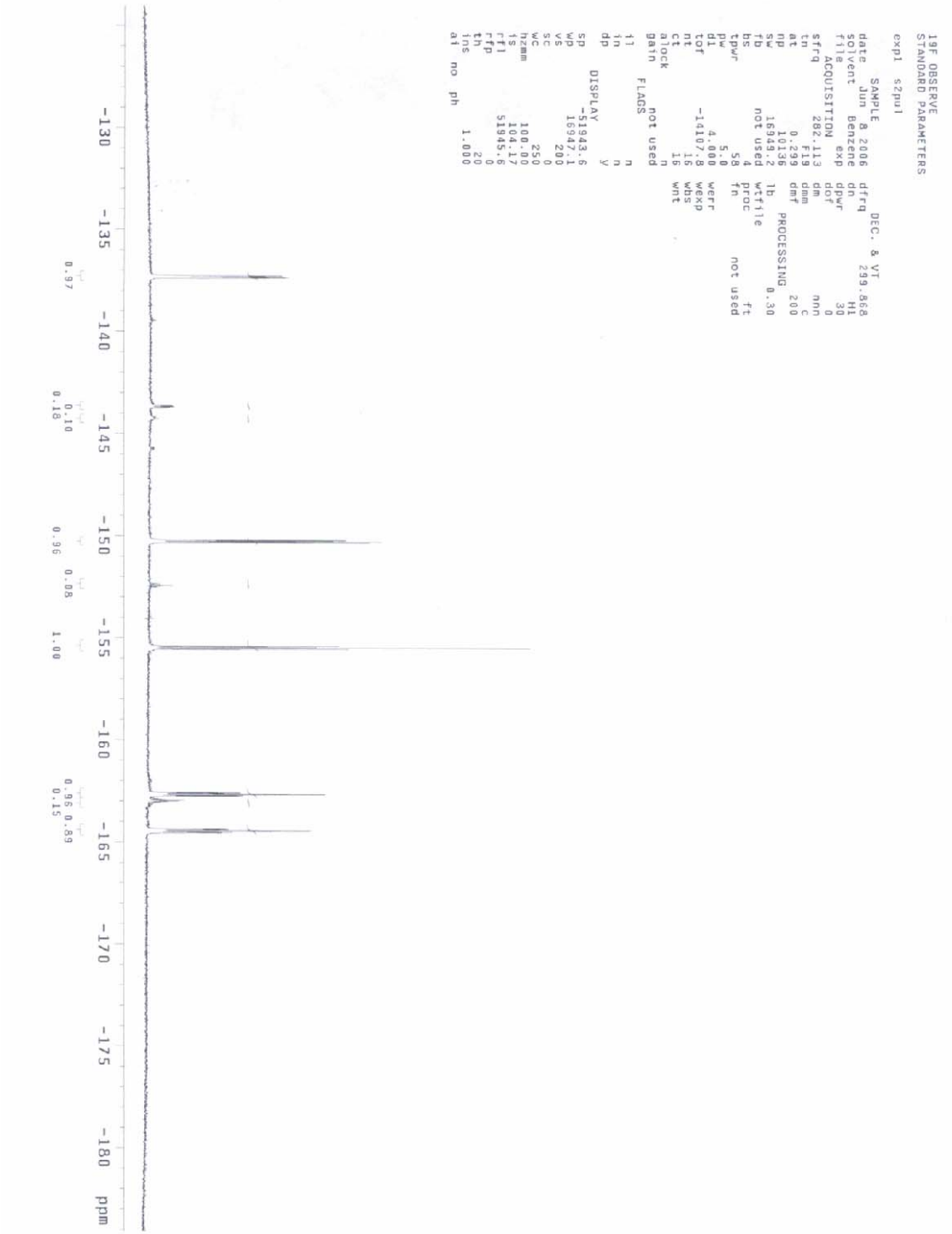


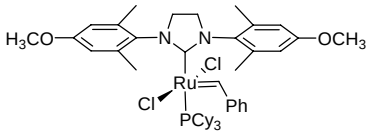
S7

^{1}H NMR Spectrum of **S7** (C_6D_6):



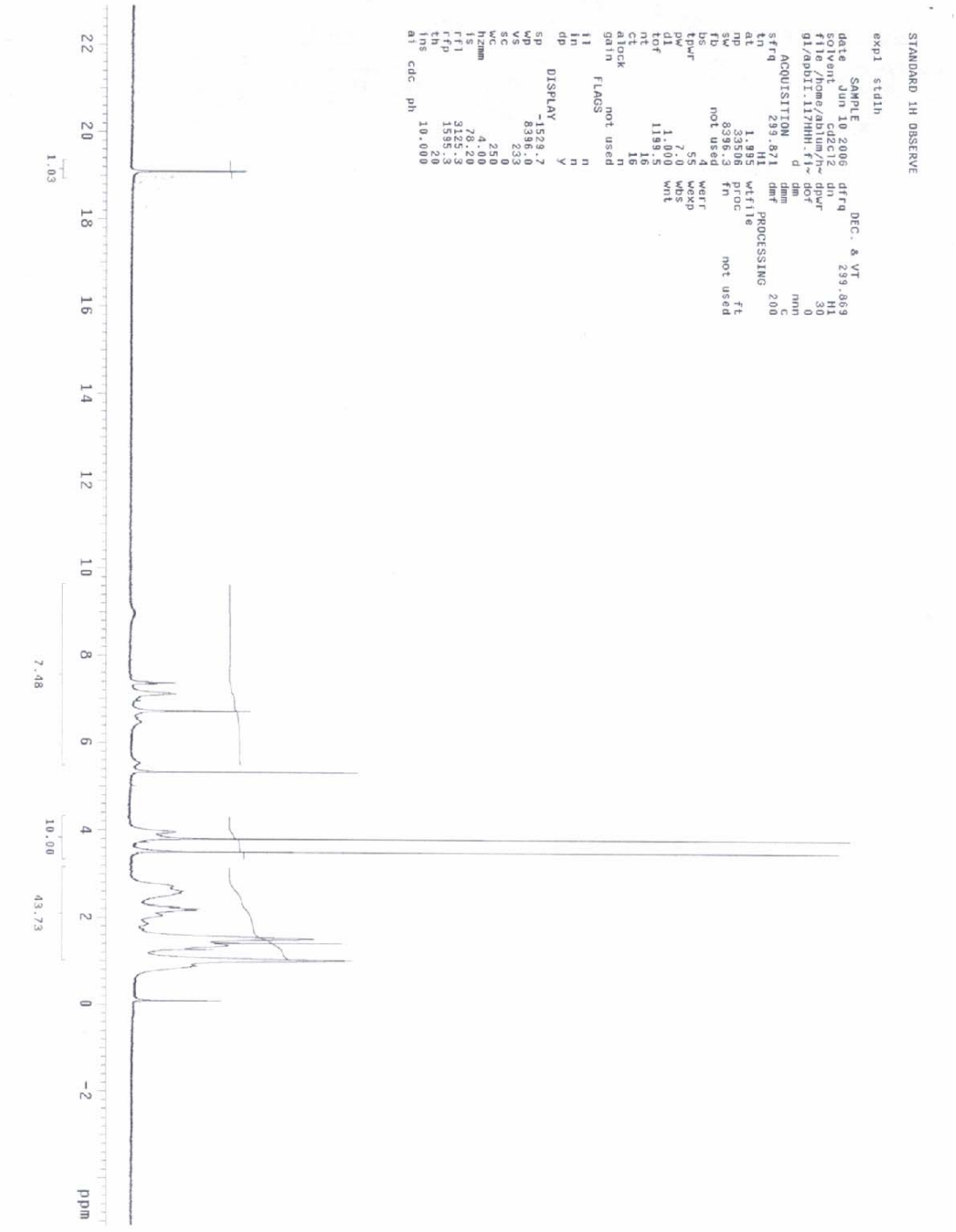
^{19}F NMR Spectrum of **S7** (C_6D_6):



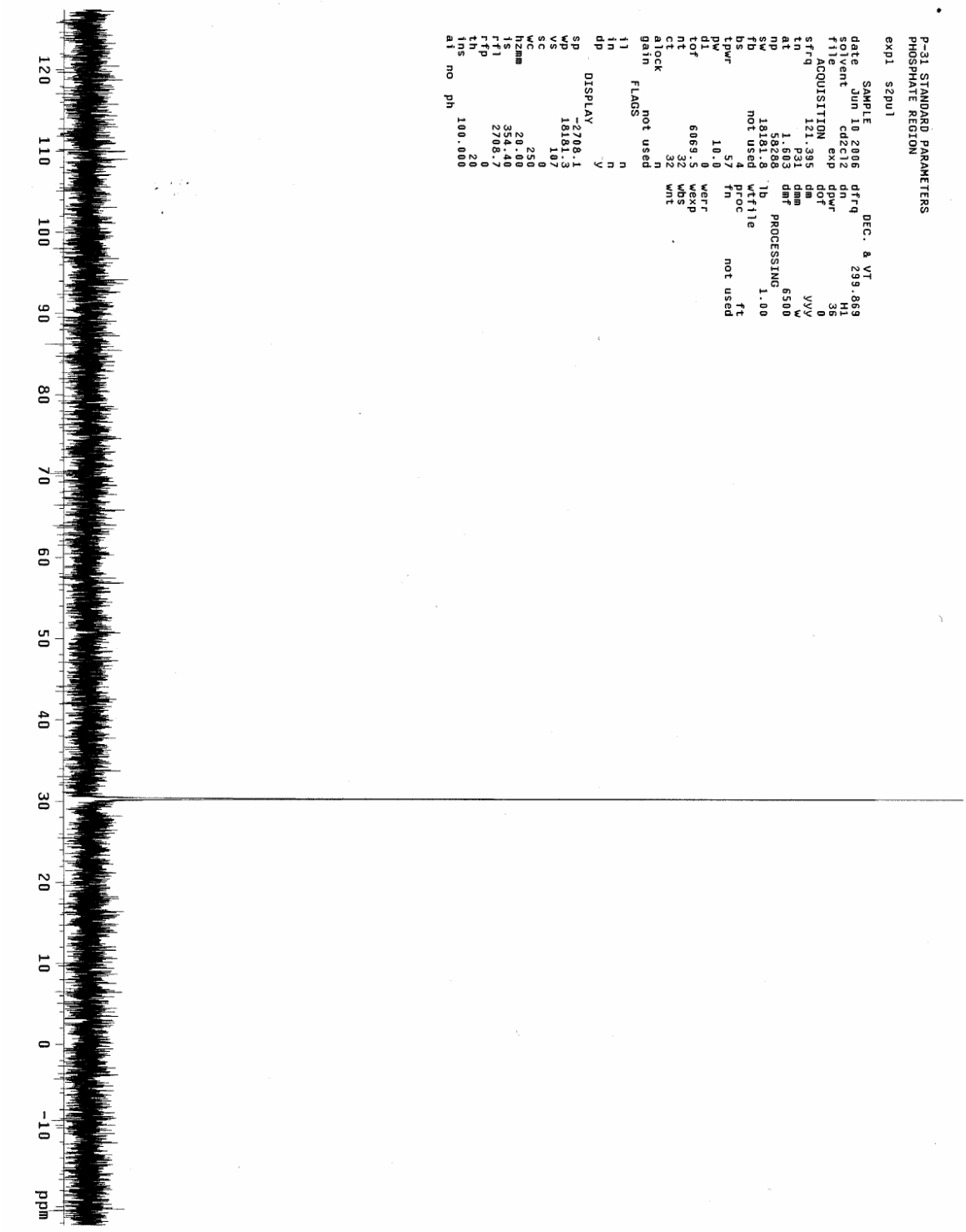


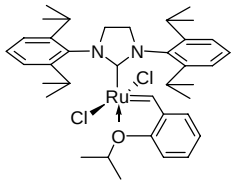
S8

^{1}H NMR Spectrum of **S8** (CD_2Cl_2):



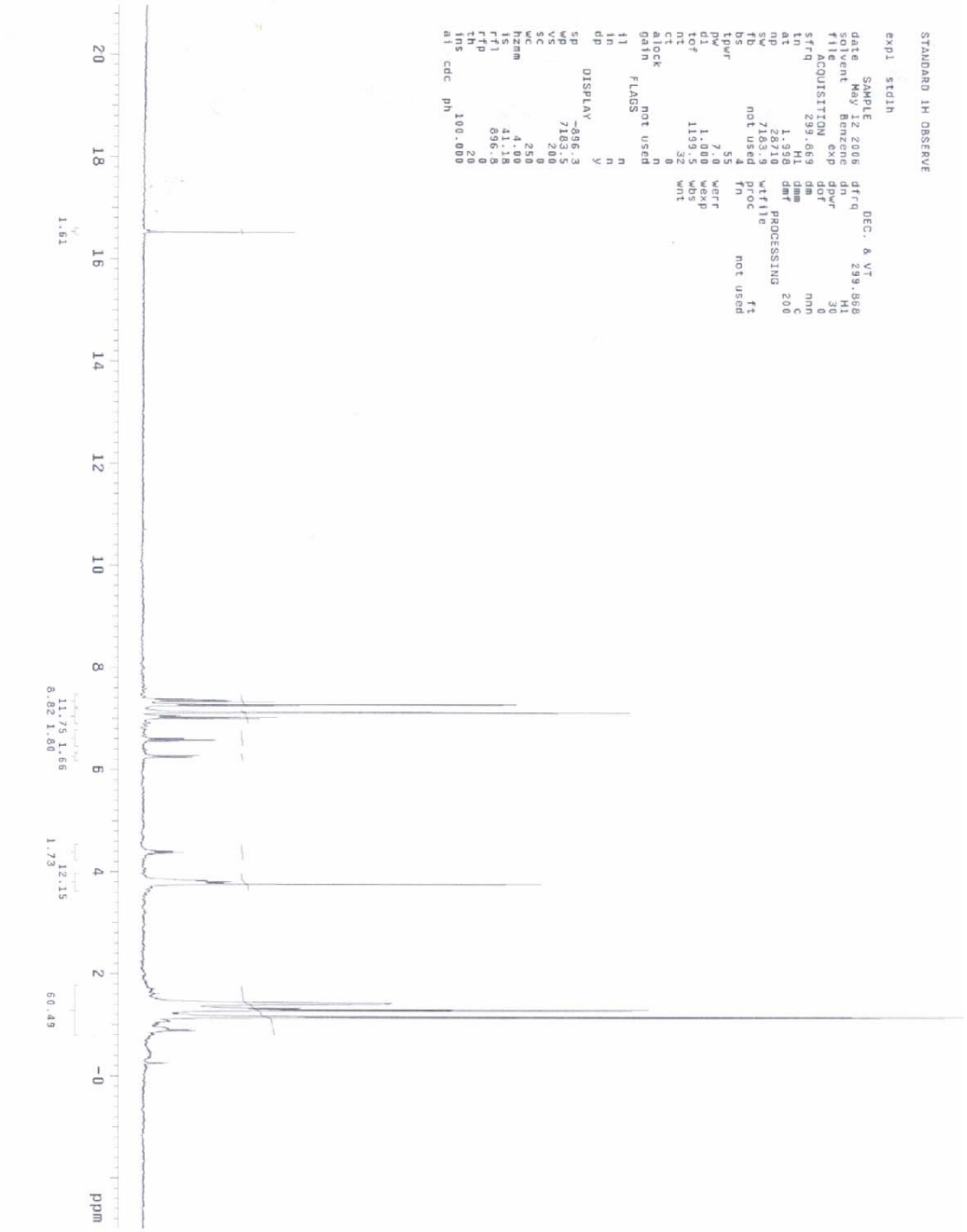
^{31}P NMR Spectrum of **S8** (CD_2Cl_2):



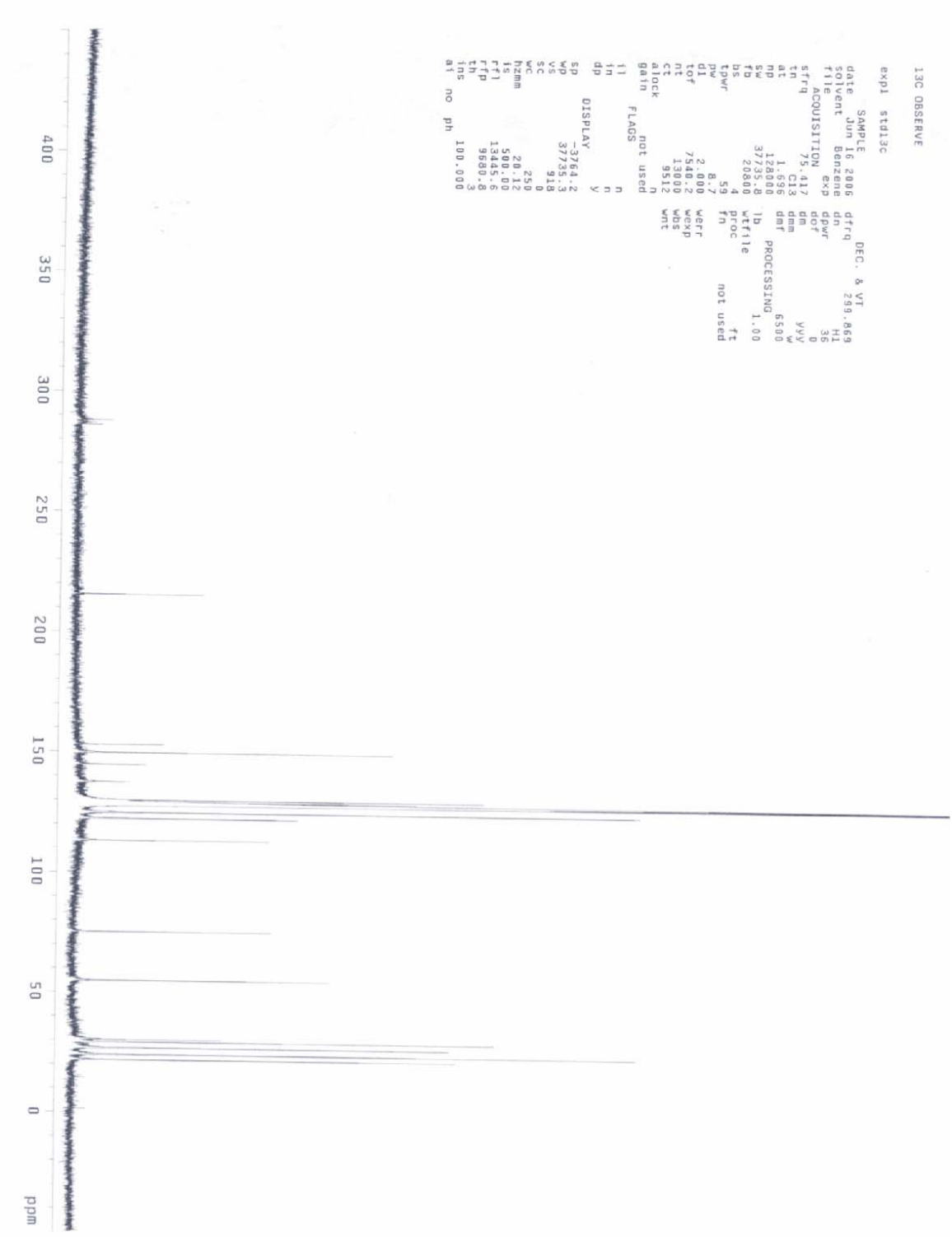


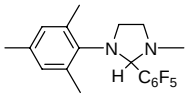
S9

^{1}H NMR Spectrum of **S9** (C_6D_6):



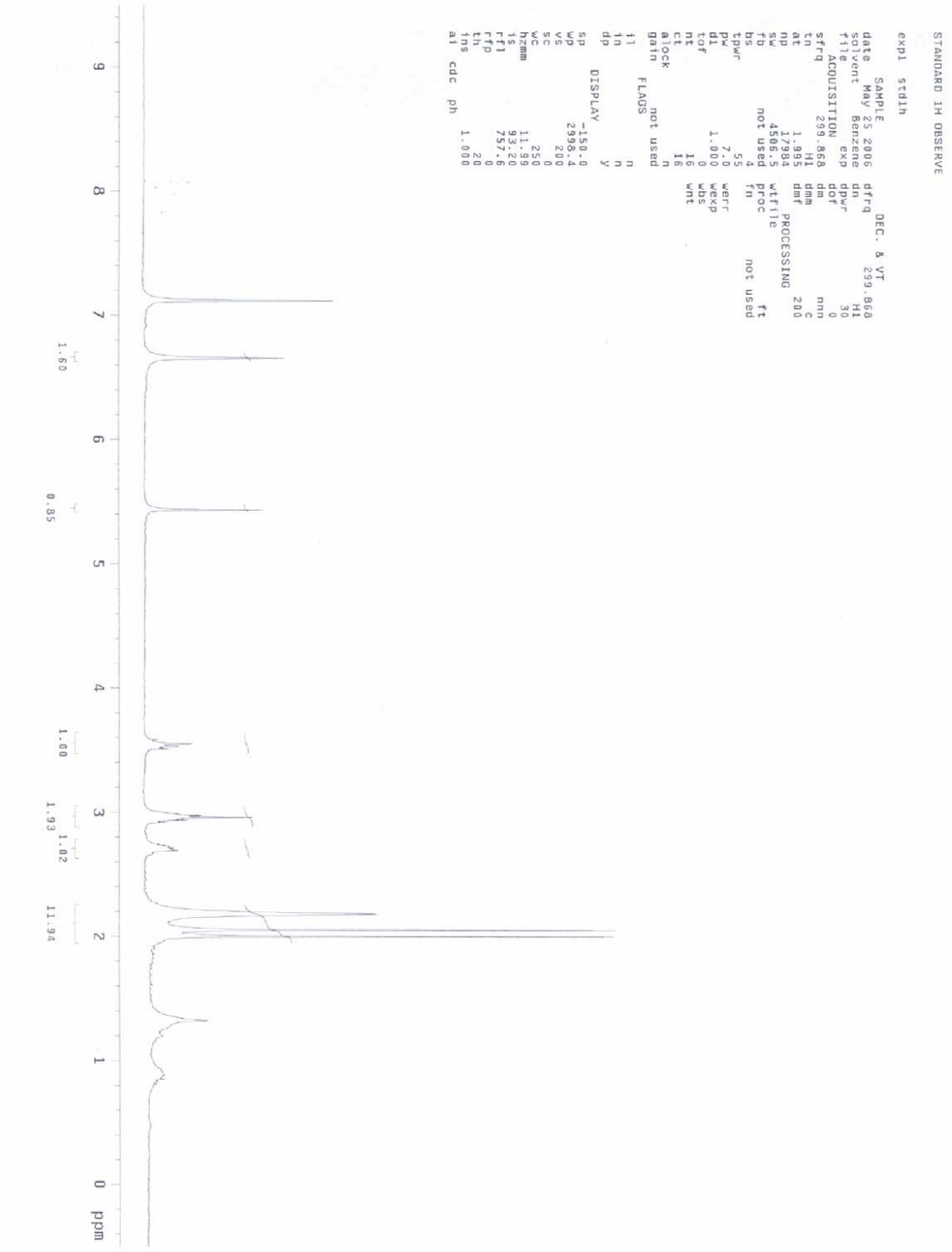
^{13}C NMR Spectrum of **S9** (C_6D_6):



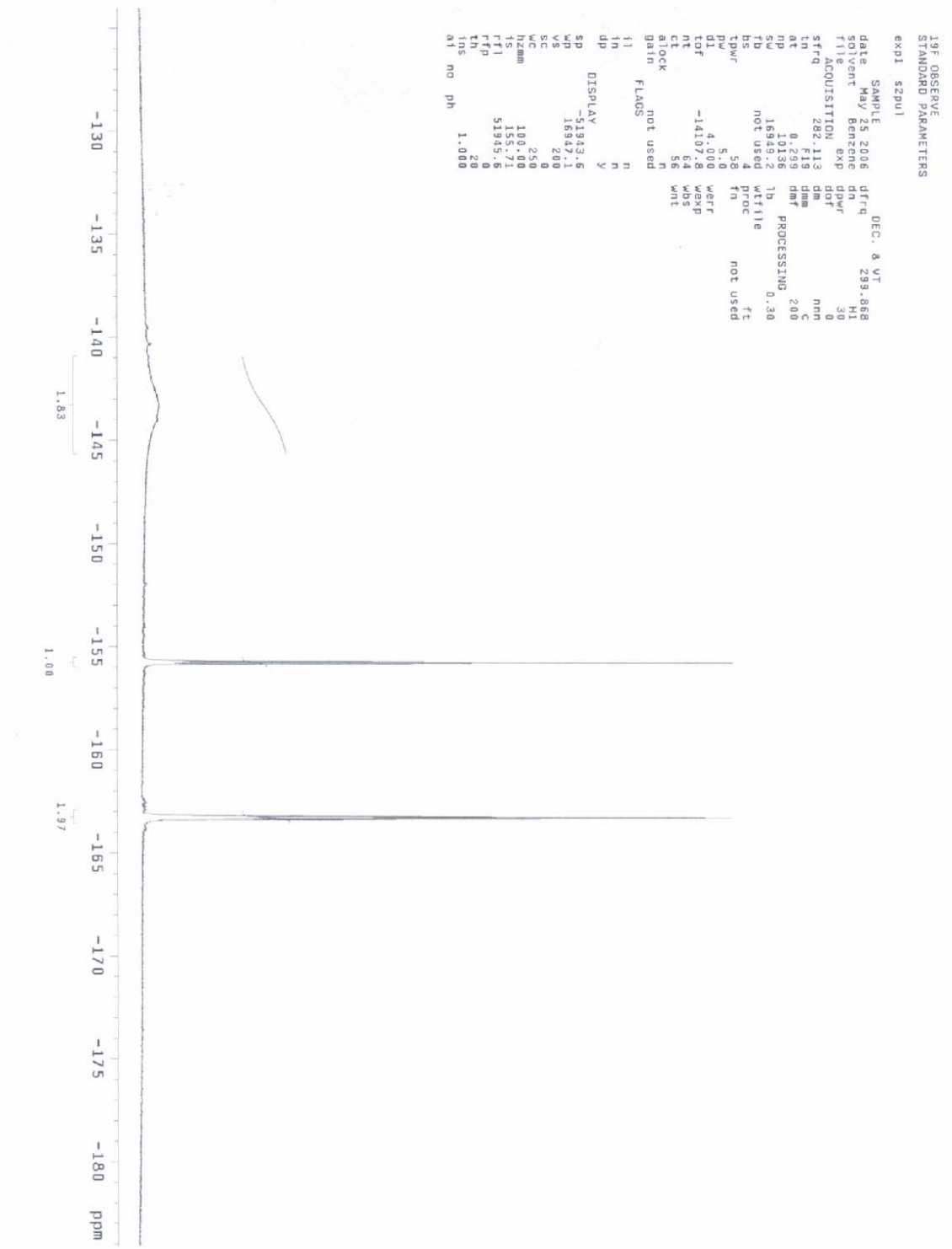


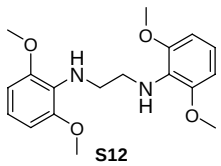
S10

^{1}H NMR Spectrum of **S10** (C_6D_6):



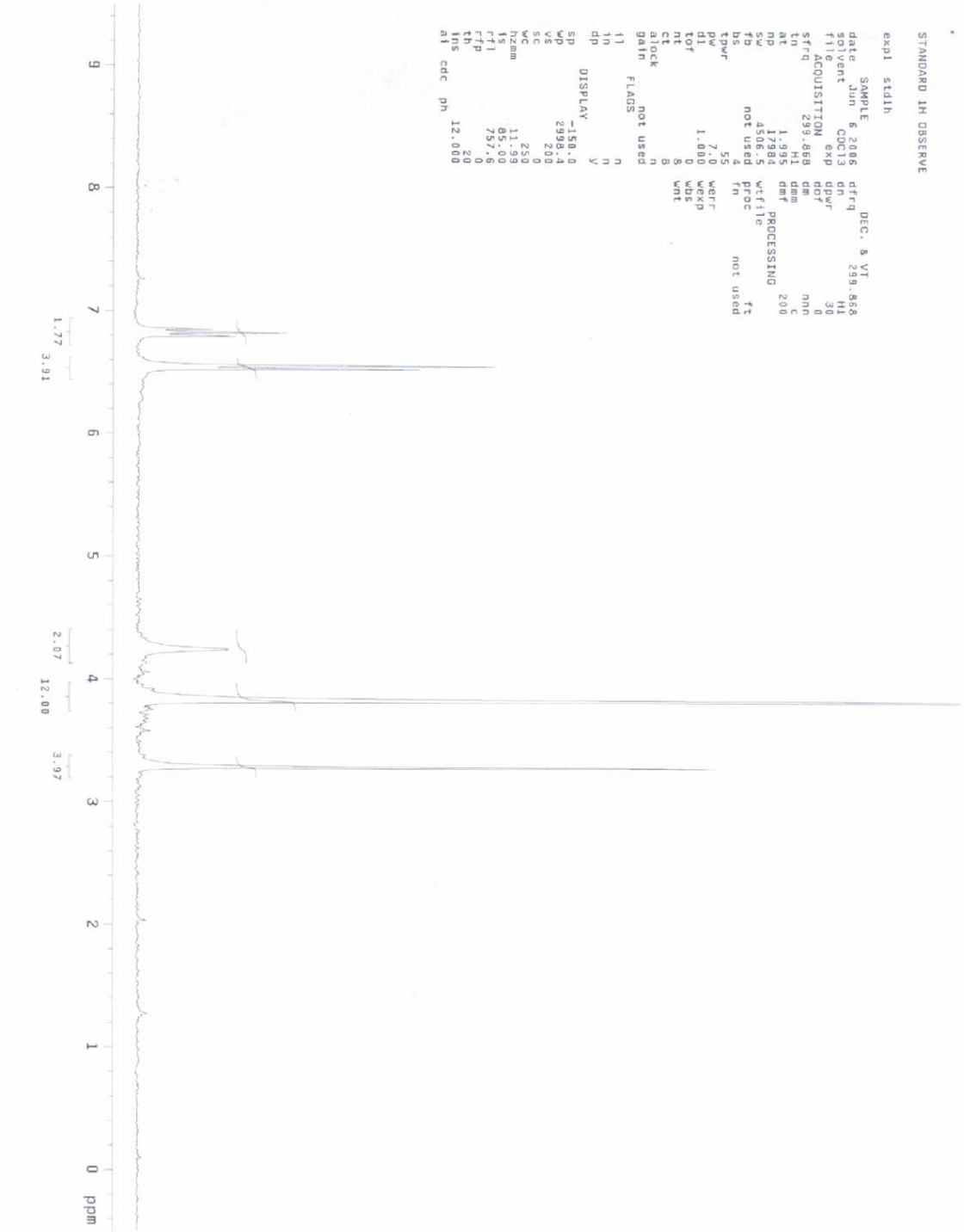
^{19}F NMR Spectrum of **S10** (C_6D_6):



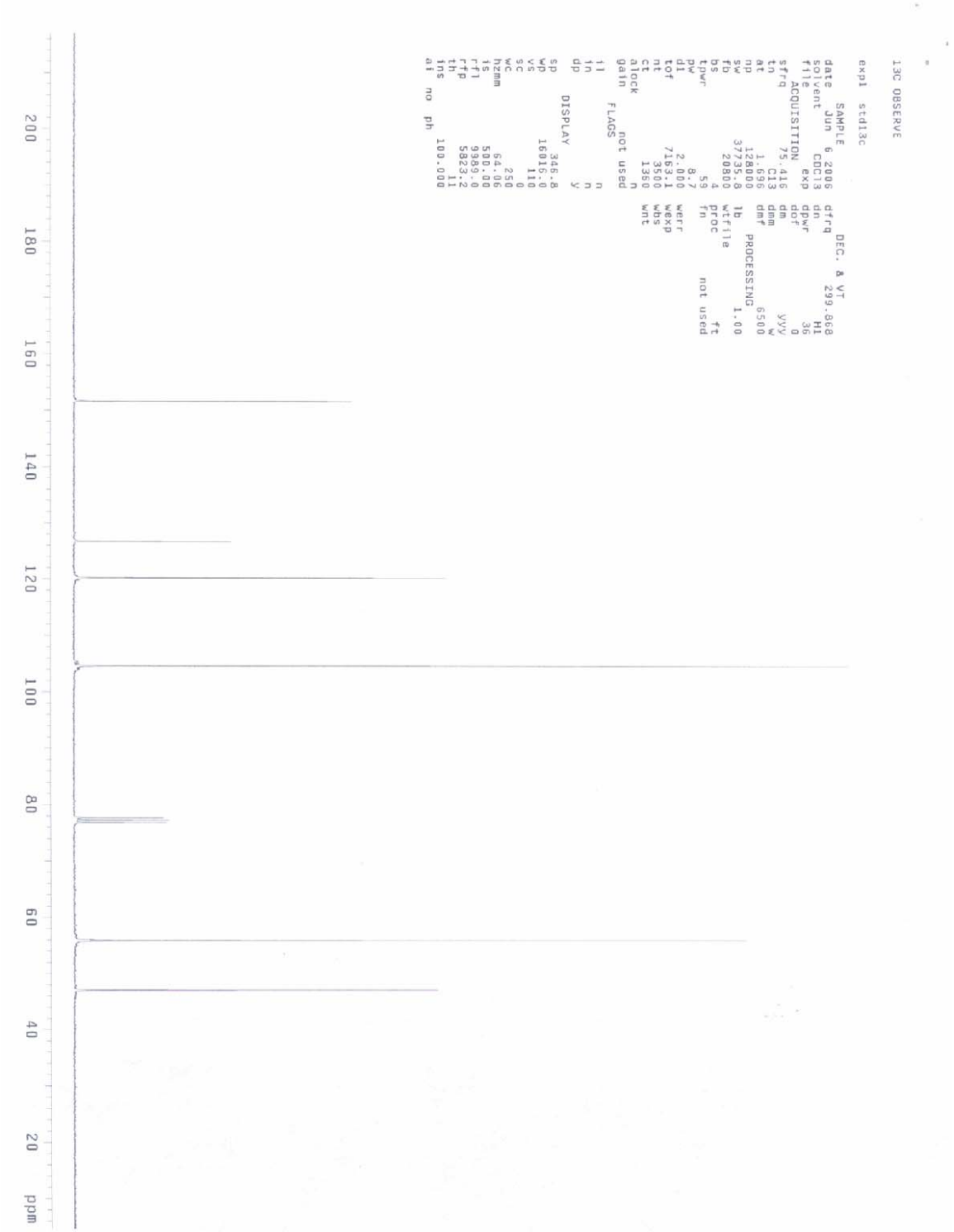


S12

^{1}H NMR Spectrum of **S12** ($CDCl_3$):

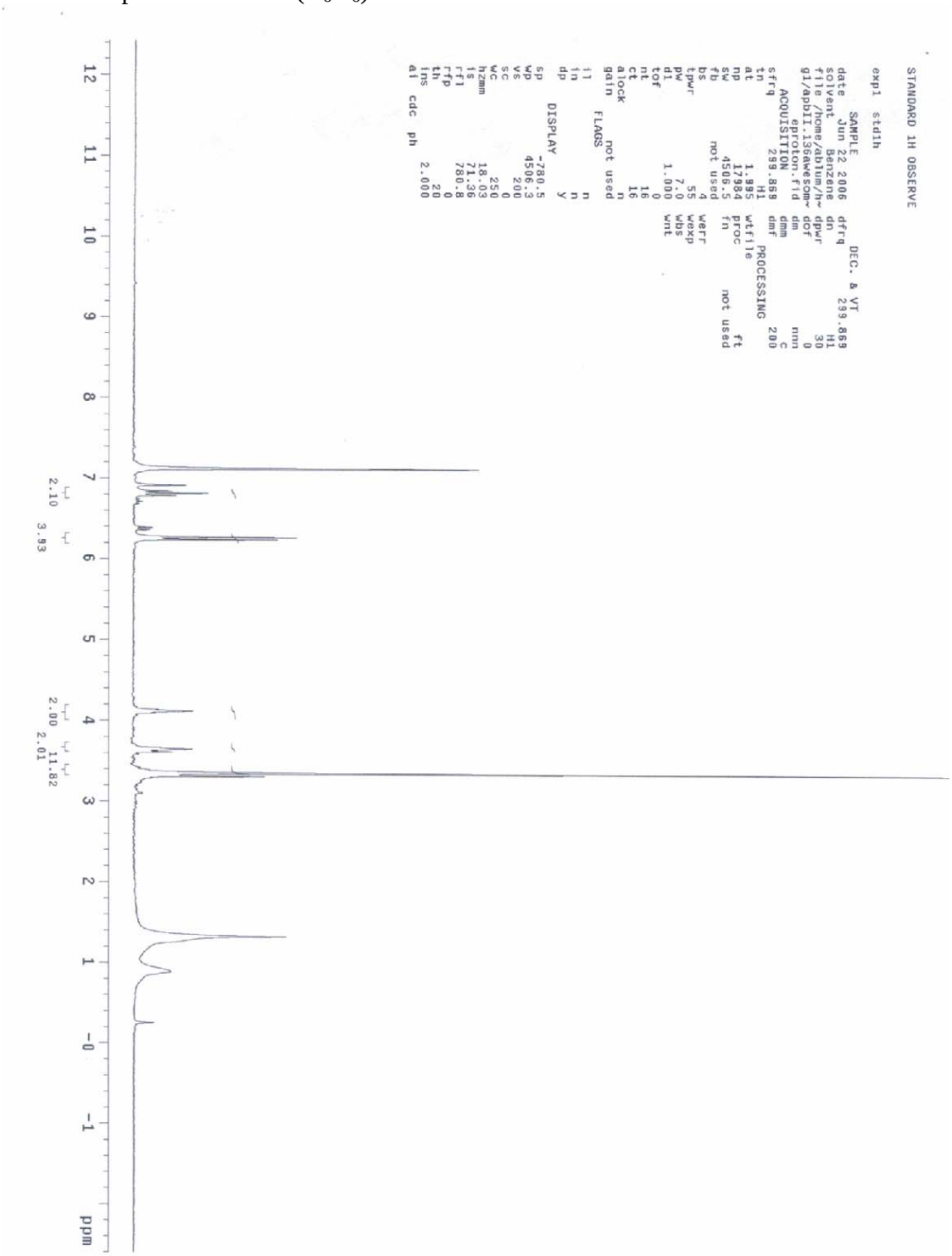


^{13}C NMR Spectrum of **S12** ($CDCl_3$):

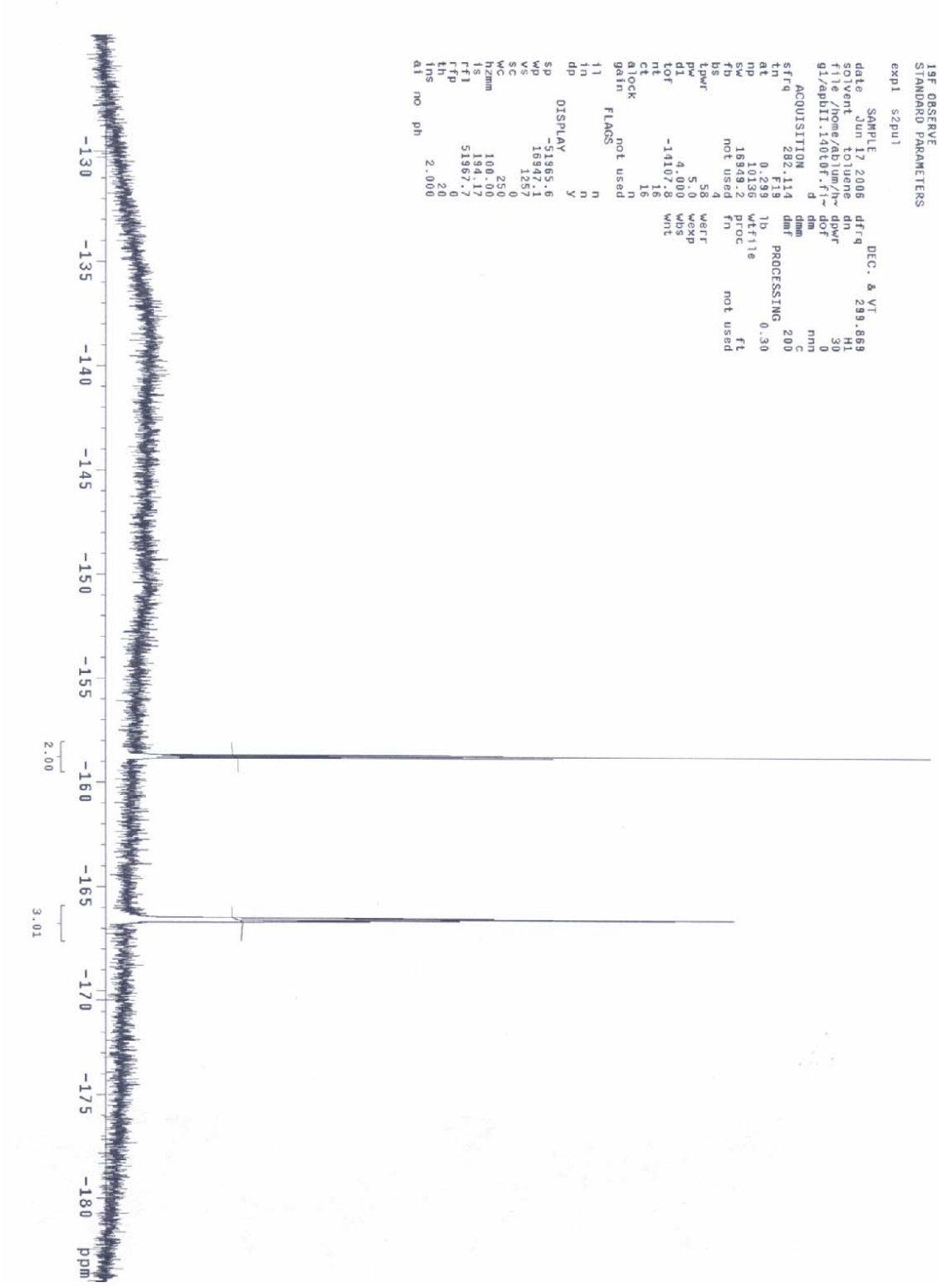


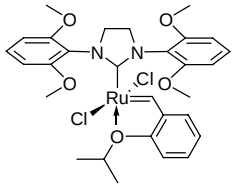
S13

^{1}H NMR Spectrum of **S13** (C_6D_6):



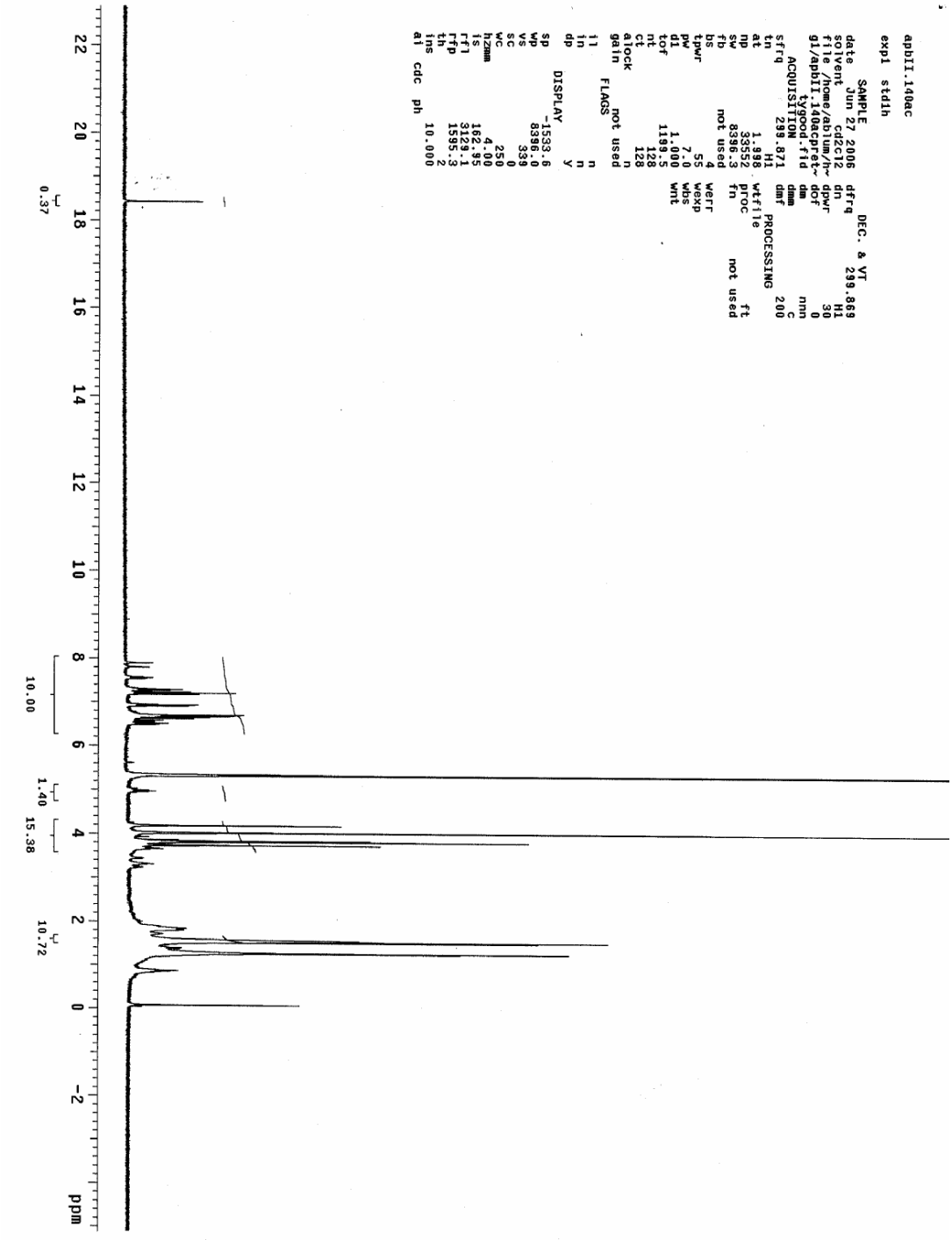
^{19}F NMR Spectrum of **S13** (C_6D_6):

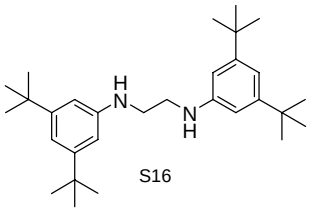




S14

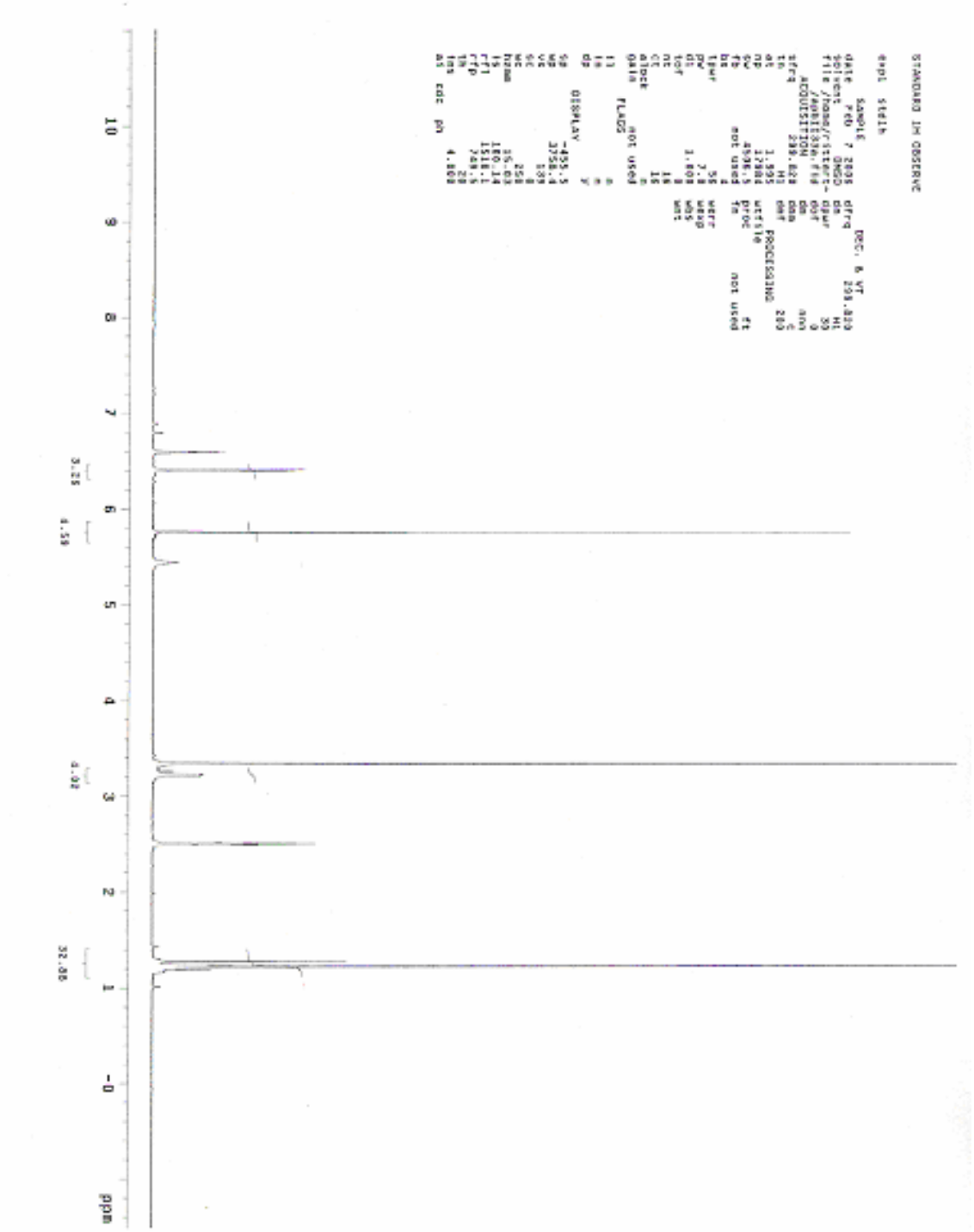
^{1}H NMR Spectrum of **S14** (CD_2Cl_2):

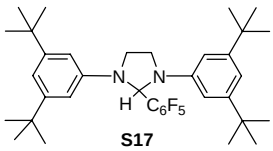




S16

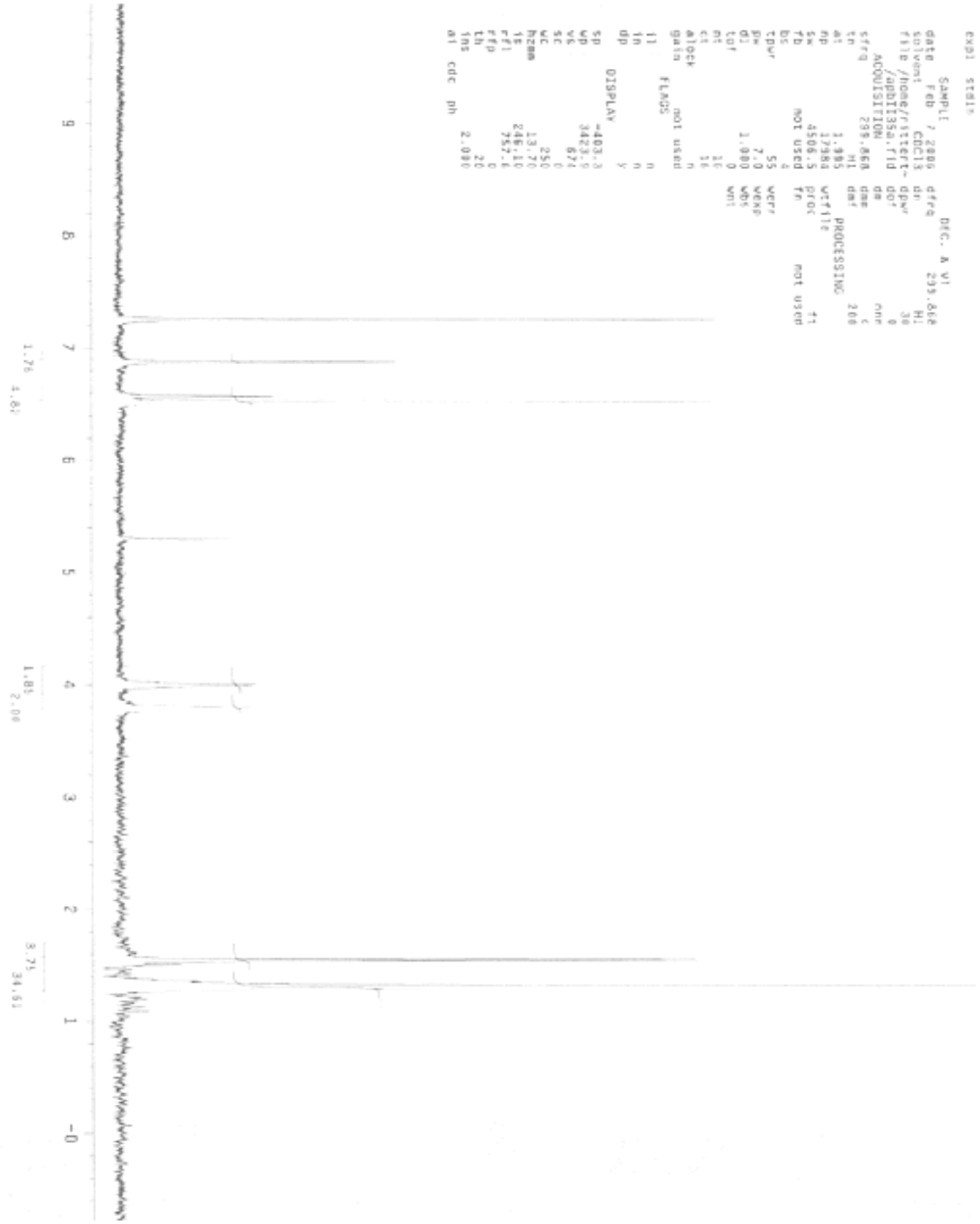
^{1}H NMR Spectrum of **S16** ($CDCl_3$):



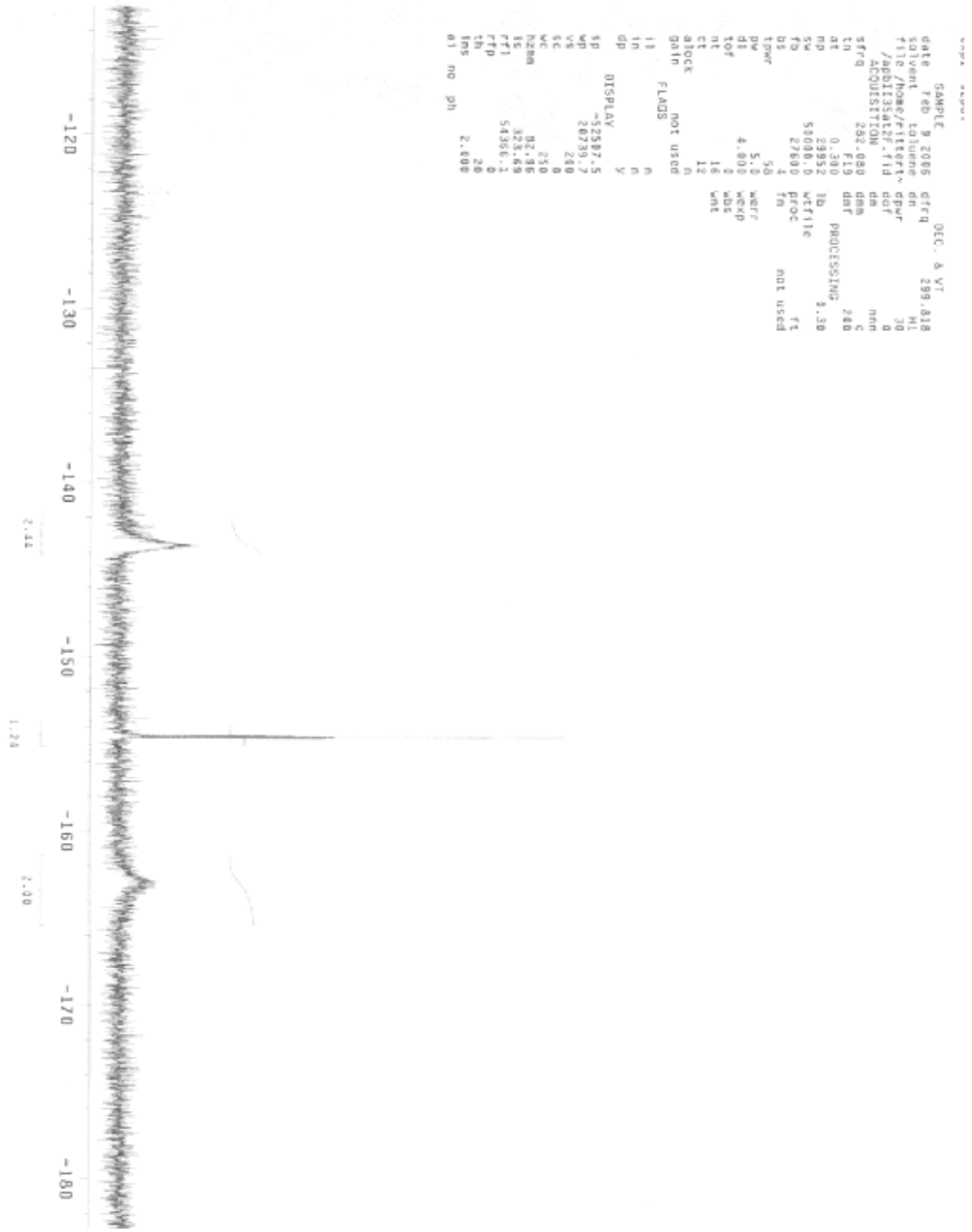


S17

^{1}H NMR Spectrum of **S17** ($CDCl_3$):



^{19}F NMR Spectrum of **S17** ($CDCl_3$):



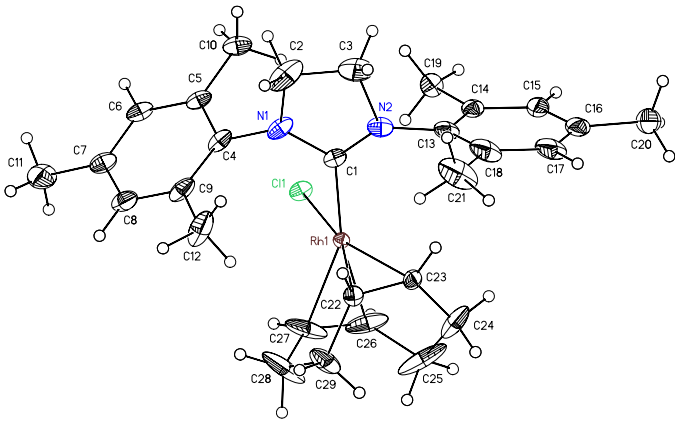
III. X-Ray Crystal Structure Analysis of S2

CALIFORNIA INSTITUTE OF TECHNOLOGY

BECKMAN INSTITUTE

X-RAY CRYSTALLOGRAPHY LABORATORY

Contents



S2

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 606520.

Table 1. Crystal data and structure refinement for S2 (CCDC 606520).

Empirical formula	$C_{29}H_{38}N_2ClRh$
Formula weight	552.97
Crystallization Solvent	Toluene/hexane
Crystal Habit	Block
Crystal size	0.29 x 0.28 x 0.20 mm^3
Crystal color	Yellow

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 41311 reflections used in lattice determination	2.21 to 49.69°
Unit cell dimensions	a = 15.3893(4) Å b = 11.8053(3) Å β= 107.3410(10)° c = 14.9767(4) Å
Volume	2597.23(12) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/c$
Density (calculated)	1.414 Mg/m^3
F(000)	1152
Data collection program	Bruker SMART v5.630
θ range for data collection	2.21 to 49.80°
Completeness to θ = 49.80°	90.5 %
Index ranges	$-32 \le h \le 23$, $-25 \le k \le 23$, $-28 \le l \le 29$
Data collection scan type	ω scans at 8 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	103676
Independent reflections	24436 [R_{int}= 0.0683]
Absorption coefficient	0.780 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.8596 and 0.8054

Table 1 (cont.)

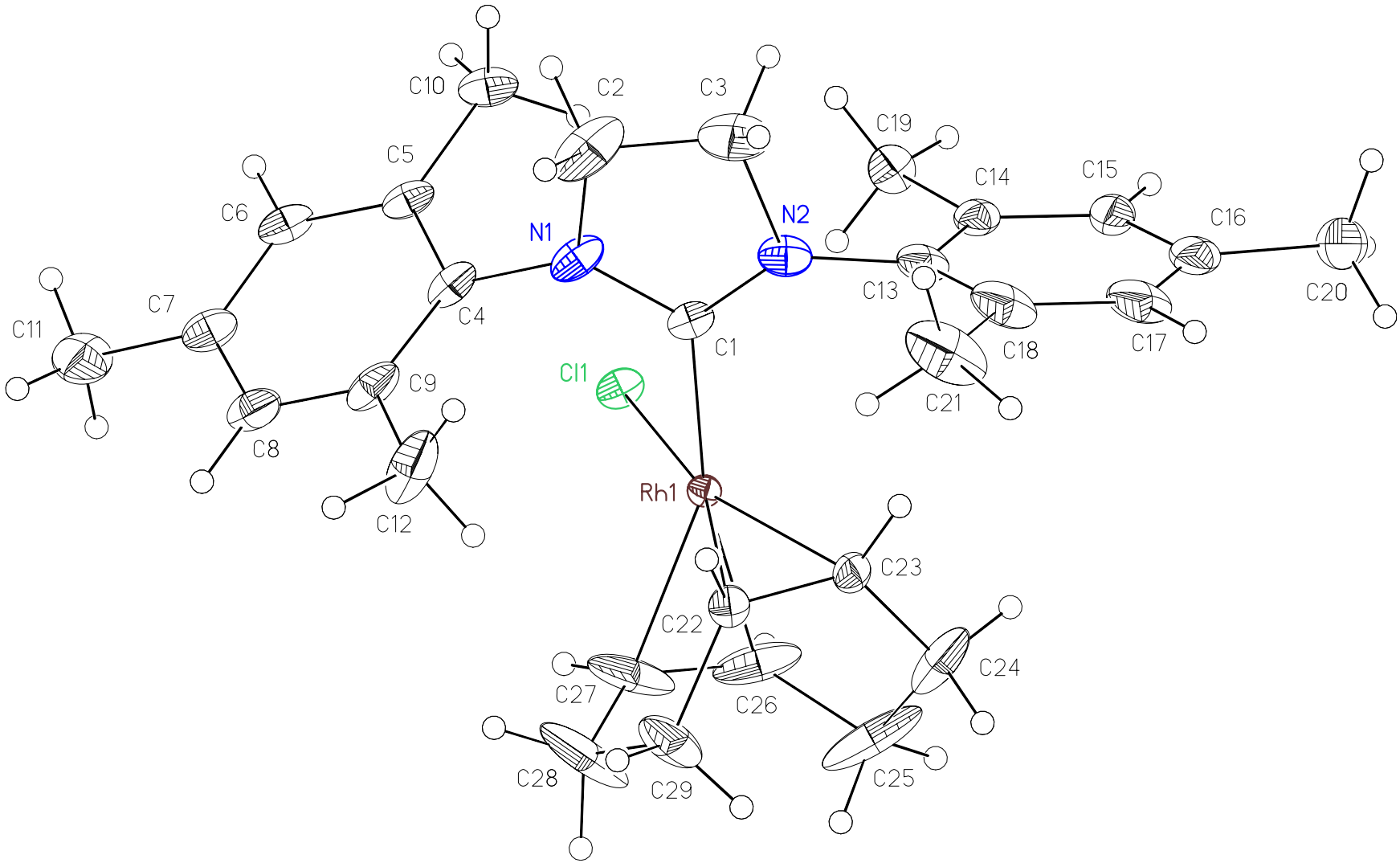
Structure solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	24436 / 0 / 304
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.034
Final R indices [$I>2\sigma(I)$, 18502 reflections]	R1 = 0.0490, *w*R2 = 0.1013
R indices (all data)	R1 = 0.0687, *w*R2 = 0.1034
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000
Largest diff. peak and hole	1.455 and -1.132 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C10
C2
C3
C19
C5
C14
C15
C6
N1
N2
C16
C13
C20
C7
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C18
C17
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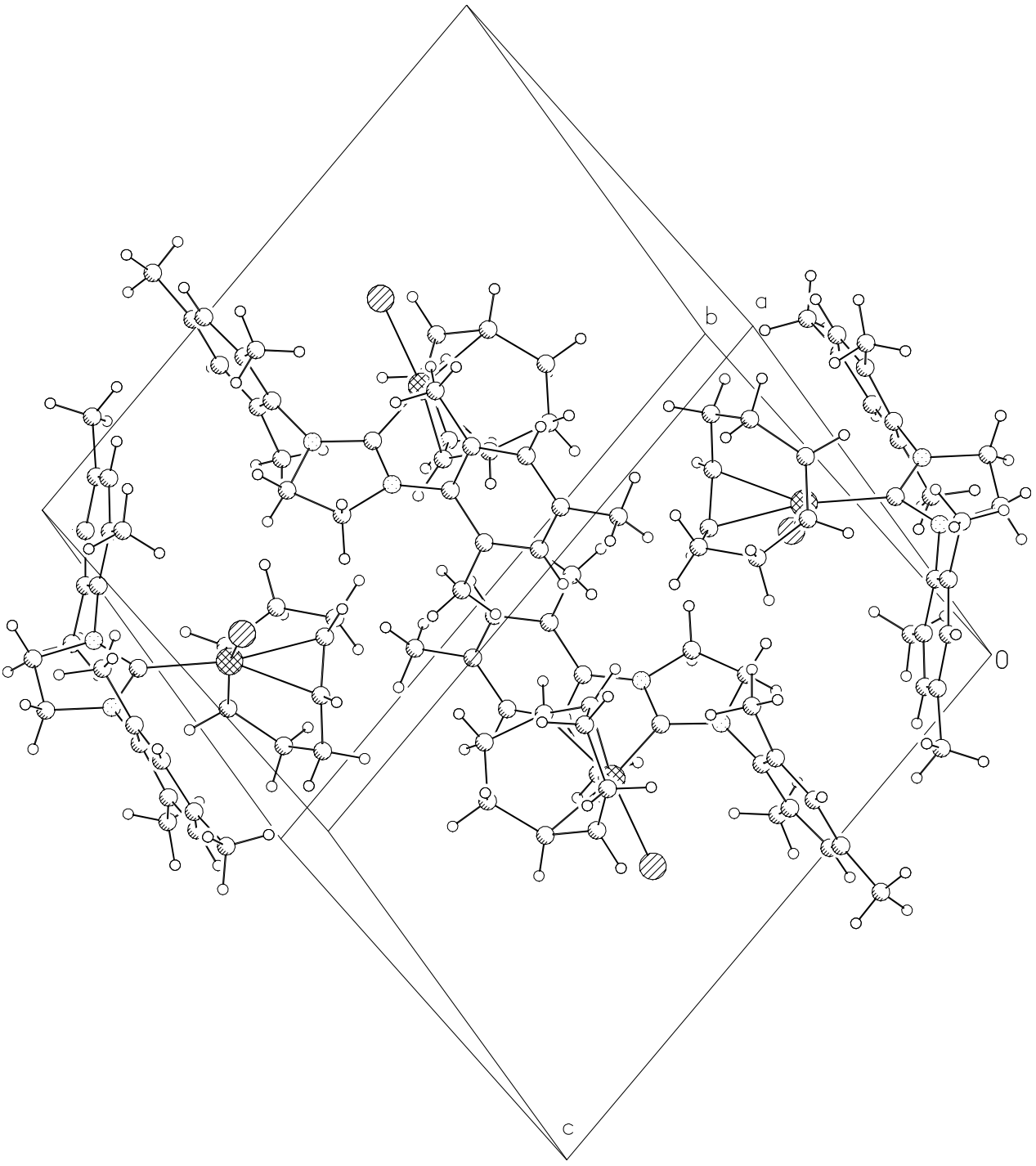
C26
C28
C29
C25


a
b
c
O

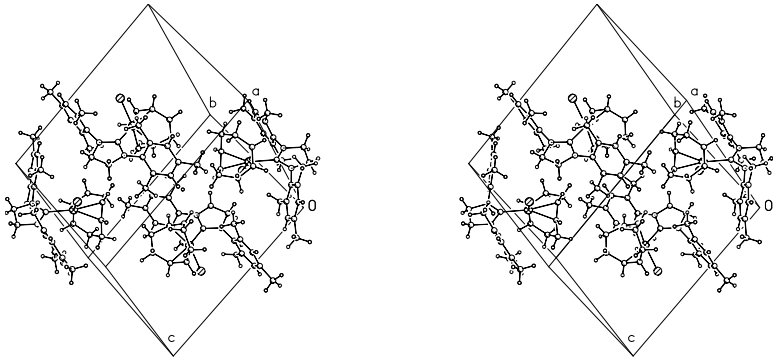

a
b
0
c
a
b
0
c

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for S2 (CCDC 606520). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Rh(1)	6967(1)	7850(1)	4210(1)	11(1)
Cl(1)	8186(1)	8789(1)	3862(1)	18(1)
N(1)	8348(1)	7704(1)	6112(1)	22(1)
N(2)	7944(1)	5997(1)	5609(1)	22(1)
C(1)	7832(1)	7109(1)	5378(1)	16(1)
C(2)	8814(2)	6992(2)	6924(1)	41(1)
C(3)	8626(2)	5810(2)	6535(1)	36(1)
C(4)	8507(1)	8907(1)	6167(1)	20(1)
C(5)	9343(1)	9302(1)	6093(1)	19(1)
C(6)	9502(1)	10470(2)	6154(1)	22(1)
C(7)	8859(1)	11235(2)	6263(1)	25(1)
C(8)	8050(1)	10807(2)	6372(1)	27(1)
C(9)	7874(1)	9647(2)	6350(1)	26(1)
C(10)	10052(1)	8528(2)	5929(1)	25(1)
C(11)	9032(2)	12495(2)	6259(2)	35(1)
C(12)	7030(1)	9217(2)	6555(2)	45(1)
C(13)	7734(1)	5054(1)	4988(1)	22(1)
C(14)	8214(1)	4893(1)	4330(1)	20(1)
C(15)	8053(1)	3912(1)	3792(1)	26(1)
C(16)	7437(1)	3093(1)	3881(2)	35(1)
C(17)	6965(1)	3275(2)	4526(2)	41(1)
C(18)	7107(1)	4237(2)	5096(2)	34(1)
C(19)	8907(1)	5743(1)	4221(1)	24(1)
C(20)	7327(2)	2012(2)	3310(2)	49(1)
C(21)	6596(2)	4399(2)	5806(2)	49(1)
C(22)	5798(1)	7449(1)	4634(1)	18(1)
C(23)	5945(1)	6601(1)	4035(1)	19(1)
C(24)	5423(1)	6441(2)	3028(1)	41(1)
C(25)	5280(2)	7524(3)	2457(1)	59(1)
C(26)	6065(1)	8352(2)	2817(1)	41(1)
C(27)	6083(1)	9186(2)	3459(2)	46(1)
C(28)	5377(2)	9404(2)	3960(3)	66(1)
C(29)	5051(1)	8325(2)	4331(2)	37(1)

Table 3. Selected bond lengths [Å] and angles [°] for S2 (CCDC 606520).

Rh(1)-C(1)	2.0513(14)	C(1)-Rh(1)-C(23)	94.49(6)
Rh(1)-C(23)	2.1150(14)	C(1)-Rh(1)-C(22)	92.43(6)
Rh(1)-C(22)	2.1316(13)	C(23)-Rh(1)-C(22)	38.67(5)
Rh(1)-C(27)	2.1664(17)	C(1)-Rh(1)-C(27)	154.24(9)
Rh(1)-C(26)	2.2153(17)	C(23)-Rh(1)-C(27)	96.53(7)
Rh(1)-Cl(1)	2.3665(3)	C(22)-Rh(1)-C(27)	81.97(6)
		C(1)-Rh(1)-C(26)	169.31(9)
		C(23)-Rh(1)-C(26)	80.50(7)
		C(22)-Rh(1)-C(26)	89.51(6)
		C(27)-Rh(1)-C(26)	36.44(10)
		C(1)-Rh(1)-Cl(1)	91.86(4)
		C(23)-Rh(1)-Cl(1)	155.30(4)
		C(22)-Rh(1)-Cl(1)	164.60(4)
		C(27)-Rh(1)-Cl(1)	87.77(5)
		C(26)-Rh(1)-Cl(1)	89.02(5)

Table 4. Bond lengths [Å] and angles [°] for S2 (CCDC 606520).

Rh(1)-C(1)	2.0513(14)	C(23)-Rh(1)-Cl(1)	155.30(4)
Rh(1)-C(23)	2.1150(14)	C(22)-Rh(1)-Cl(1)	164.60(4)
Rh(1)-C(22)	2.1316(13)	C(27)-Rh(1)-Cl(1)	87.77(5)
Rh(1)-C(27)	2.1664(17)	C(26)-Rh(1)-Cl(1)	89.02(5)
Rh(1)-C(26)	2.2153(17)	C(1)-N(1)-C(4)	127.62(13)
Rh(1)-Cl(1)	2.3665(3)	C(1)-N(1)-C(2)	113.54(14)
N(1)-C(1)	1.3455(19)	C(4)-N(1)-C(2)	118.81(14)
N(1)-C(4)	1.439(2)	C(1)-N(2)-C(13)	127.06(12)
N(1)-C(2)	1.476(2)	C(1)-N(2)-C(3)	112.55(15)
N(2)-C(1)	1.3557(19)	C(13)-N(2)-C(3)	116.98(14)
N(2)-C(13)	1.425(2)	N(1)-C(1)-N(2)	107.29(12)
N(2)-C(3)	1.485(2)	N(1)-C(1)-Rh(1)	123.32(11)
C(2)-C(3)	1.507(3)	N(2)-C(1)-Rh(1)	129.16(11)
C(4)-C(9)	1.395(2)	N(1)-C(2)-C(3)	102.62(14)
C(4)-C(5)	1.4032(19)	N(2)-C(3)-C(2)	102.93(15)
C(5)-C(6)	1.400(2)	C(9)-C(4)-C(5)	121.14(15)
C(5)-C(10)	1.499(2)	C(9)-C(4)-N(1)	120.89(13)
C(6)-C(7)	1.386(2)	C(5)-C(4)-N(1)	117.84(14)
C(7)-C(8)	1.397(2)	C(6)-C(5)-C(4)	118.02(15)
C(7)-C(11)	1.511(3)	C(6)-C(5)-C(10)	119.30(14)
C(8)-C(9)	1.394(3)	C(4)-C(5)-C(10)	122.67(15)
C(9)-C(12)	1.510(2)	C(7)-C(6)-C(5)	122.16(15)
C(13)-C(18)	1.408(2)	C(6)-C(7)-C(8)	118.11(17)
C(13)-C(14)	1.409(2)	C(6)-C(7)-C(11)	120.47(17)
C(14)-C(15)	1.391(2)	C(8)-C(7)-C(11)	121.42(18)
C(14)-C(19)	1.509(2)	C(9)-C(8)-C(7)	121.70(17)
C(15)-C(16)	1.388(3)	C(8)-C(9)-C(4)	118.59(14)
C(16)-C(17)	1.388(3)	C(8)-C(9)-C(12)	119.87(17)
C(16)-C(20)	1.517(3)	C(4)-C(9)-C(12)	121.51(18)
C(17)-C(18)	1.398(3)	C(18)-C(13)-C(14)	120.53(17)
C(18)-C(21)	1.511(3)	C(18)-C(13)-N(2)	119.37(16)
C(22)-C(23)	1.406(2)	C(14)-C(13)-N(2)	119.83(14)
C(22)-C(29)	1.512(2)	C(15)-C(14)-C(13)	118.55(15)
C(23)-C(24)	1.494(2)	C(15)-C(14)-C(19)	120.01(15)
C(24)-C(25)	1.517(4)	C(13)-C(14)-C(19)	121.42(14)
C(25)-C(26)	1.522(3)	C(16)-C(15)-C(14)	122.18(18)
C(26)-C(27)	1.371(4)	C(15)-C(16)-C(17)	118.26(19)
C(27)-C(28)	1.515(3)	C(15)-C(16)-C(20)	119.8(2)
C(28)-C(29)	1.533(3)	C(17)-C(16)-C(20)	121.93(19)
		C(16)-C(17)-C(18)	122.13(17)
C(1)-Rh(1)-C(23)	94.49(6)	C(13)-C(18)-C(17)	118.32(18)
C(1)-Rh(1)-C(22)	92.43(6)	C(13)-C(18)-C(21)	120.8(2)
C(23)-Rh(1)-C(22)	38.67(5)	C(17)-C(18)-C(21)	120.85(18)
C(1)-Rh(1)-C(27)	154.24(9)	C(23)-C(22)-C(29)	123.24(16)
C(23)-Rh(1)-C(27)	96.53(7)	C(23)-C(22)-Rh(1)	70.03(8)
C(22)-Rh(1)-C(27)	81.97(6)	C(29)-C(22)-Rh(1)	113.17(10)
C(1)-Rh(1)-C(26)	169.31(9)	C(22)-C(23)-C(24)	126.36(16)
C(23)-Rh(1)-C(26)	80.50(7)	C(22)-C(23)-Rh(1)	71.30(8)
C(22)-Rh(1)-C(26)	89.51(6)	C(24)-C(23)-Rh(1)	111.68(12)
C(27)-Rh(1)-C(26)	36.44(10)	C(23)-C(24)-C(25)	114.01(18)
C(1)-Rh(1)-Cl(1)	91.86(4)	C(24)-C(25)-C(26)	112.03(16)

C(27)-C(26)-C(25)	123.9(2)	C(26)-C(27)-Rh(1)	73.72(11)
C(27)-C(26)-Rh(1)	69.84(11)	C(28)-C(27)-Rh(1)	107.40(14)
C(25)-C(26)-Rh(1)	111.74(13)	C(27)-C(28)-C(29)	113.52(17)
C(26)-C(27)-C(28)	127.0(2)	C(22)-C(29)-C(28)	112.01(15)

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for S2 (CCDC 606520). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	105(1)	120(1)	121(1)	7(1)	44(1)	0(1)
Cl(1)	146(1)	237(1)	166(1)	33(1)	66(1)	-33(1)
N(1)	193(5)	347(7)	113(5)	37(4)	24(4)	-74(5)
N(2)	221(6)	246(6)	177(5)	101(4)	52(4)	35(4)
C(1)	136(5)	238(5)	125(5)	34(4)	51(3)	-16(5)
C(2)	438(12)	546(13)	153(7)	163(7)	-38(6)	-199(9)
C(3)	353(10)	513(12)	199(8)	175(7)	49(7)	127(9)
C(4)	154(6)	344(7)	115(5)	-27(4)	55(4)	-83(5)
C(5)	134(5)	324(7)	113(5)	35(4)	30(4)	-28(5)
C(6)	150(6)	325(7)	165(6)	71(5)	20(4)	-45(5)
C(7)	223(7)	348(8)	148(6)	51(5)	-6(5)	-3(6)
C(8)	172(7)	432(10)	198(7)	-62(6)	28(5)	9(6)
C(9)	145(6)	483(10)	181(7)	-114(6)	73(5)	-86(6)
C(10)	160(6)	377(9)	220(7)	68(6)	60(5)	22(6)
C(11)	373(11)	303(8)	313(9)	124(7)	1(7)	32(8)
C(12)	271(9)	691(15)	497(13)	-381(11)	271(9)	-242(10)
C(13)	178(6)	174(5)	309(8)	114(5)	72(5)	27(5)
C(14)	170(6)	175(5)	228(6)	61(4)	14(5)	9(4)
C(15)	237(8)	194(6)	280(8)	24(5)	-16(6)	25(5)
C(16)	213(8)	159(6)	573(13)	56(6)	-54(8)	21(5)
C(17)	198(8)	182(7)	803(16)	173(8)	96(9)	6(6)
C(18)	245(8)	210(7)	606(13)	199(7)	189(8)	44(6)
C(19)	246(7)	225(6)	258(8)	18(5)	112(6)	-16(5)
C(20)	318(11)	208(8)	792(18)	-46(9)	-56(11)	-23(7)
C(21)	437(13)	339(10)	846(19)	303(11)	407(14)	71(9)
C(22)	157(6)	191(5)	213(6)	-11(4)	95(4)	-25(4)
C(23)	143(6)	176(5)	239(6)	-32(4)	60(4)	-34(4)
C(24)	248(9)	712(15)	282(9)	-246(9)	109(7)	-239(10)
C(25)	241(9)	1280(30)	180(8)	182(11)	-56(6)	-295(13)
C(26)	161(7)	744(16)	281(9)	307(10)	6(6)	-37(8)
C(27)	222(8)	355(10)	868(18)	414(11)	250(10)	151(7)
C(28)	438(14)	258(9)	1480(30)	324(14)	607(18)	209(9)
C(29)	247(8)	259(8)	695(15)	69(8)	301(10)	71(7)